U.S. DEPARTMENT OF COMMERCE
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PB-279 872

Removal and Recovery of Sulfide from Tannery Wastewater

Blueside Co, Inc, St Joseph, Mo

Prepared for

Industrial Environmental Research Lab -Cincinnati, Ohio

Dec 77

EPA-600/2-77-031
December 1977

PB 279 872
Environmental Protection Technology Series

REMOVAL AND RECOVERY OF SULFIDE FROM TANNERY WASTEWATER

Industrial Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

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TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-600/2-77-031

2.

3. RECIPIENT'S ACCESSION NO.
PB279872

4. TITLE AND SUBTITLE
REMOVAL AND RECOVERY OF SULFIDE FROM TANNERY WASTEWATER

5. REPORT DATE
December 1977 issuing date

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
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Roger J. Langlais

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
The Blueside Company, Inc.
Box 383
St. Joseph, Missouri 64502

10. PROGRAM ELEMENT NO.
1DB610

11. CONTRACT/GRANT NO.
12120 EPC

12. SPONSORING AGENCY NAME AND ADDRESS
Industrial Environmental Research Laboratory-Cin., OH
Office of Research & Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

13. TYPE OF REPORT AND PERIOD COVERED
R&D (1970-1975)

14. SPONSORING AGENCY CODE
EPA/600/12

15. SUPPLEMENTARY NOTES
Contact: Jack Witherow, FTS-420-4793

16. ABSTRACT

Recovery of sulfide from tannery waste was accomplished through acidification with sulfuric acid in a closed system and removing hydrogen sulfide formed by blowing with air. Sulfide was then absorbed in caustic solution to produce re-usable sodium sulfide/sulfhydrate liquor for the tanning un-hairing process. Plant scale equipment was used in demonstration. The recovered sulfide was reused at the tannery and resulted in an annual savings of $397,437 for chemicals. The annual cost of the recovery system was $305,385. Operational difficulties, design modifications, and cost effectiveness are discussed in detail. Protein recovery is recognized as an adjunct to the acidification procedure and significant reduction in BOD loading is achievable by subsequent clarification.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Leather, Tanning Materials	Leather Industry, Waste Abatement, Process Modification, Engineering Design, Sulfide Recovery, Sulfide Destruction, Waste Characterization and Loading	13B

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 142
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE A07-A01

EPA Form 2220-1 (9-73)

☆ U.S. GOVERNMENT PRINTING OFFICE 1977 — 757-140/6671

EPA-600/2-77-031
December 1977

REMOVAL AND RECOVERY OF SULFIDE FROM TANNERY WASTEWATER

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Grant No. 12120 EPC

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FOREWORD

When energy and material resources are extracted, processed, converted, and used the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report describes technology for in-plant process change to remove a major pollutant from tanning wastewater and recovery and reuse of a chemical. The purpose of the project was to demonstrate the technical and economical feasibility of a physical-chemical process. Also described in the report is the development of the equipment design.

The report will be of interest to all tanners who have a beamhouse, to engineering consultants and to municipalities that receive wastewater from beamhouse operations.

Further information on the subject can be obtained from the Food and Wood Products Branch, Corvallis Field Station, Industrial Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Corvallis, Oregon.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

PREFACE

One of the major components of the effluent from the tanning industry is sulfides. The leather industry uses large quantities of sulfides, 1 - 5% based on the hide weight. These sulfides present a serious disposal problem. When discharged into a river or stream, they cause a drastic reduction in dissolved oxygen, the formation of dark-colored precipitates with iron and other minerals present in the water, and, in an acid media, cause a disagreeable odor. Toxic hydrogen sulfide may be formed when mixed with acidic wastes.

Sulfide can be removed from tannery effluent slowly by aeration or more rapidly by air oxidation through the use of a manganese sulfate catalyst. Sulfides in a secondary treatment system decrease the effectiveness of the aeration due to the consumption of oxygen and may result in the release of hydrogen sulfide to the atmosphere. Catalytic chemical oxidation of the sulfide with air results in a quantitative removal of the sulfide. The process, though effective, is time consuming and expensive in chemicals and power.

The purpose of this demonstration grant was to determine the practicality of a sulfide removal-recovery system. The system is based on the removal of the sulfide as hydrogen sulfide gas from the clarified acidified wastewater. The hydrogen sulfide gas released is absorbed in sodium hydroxide, forming a solution of sodium sulfide which is re-used in the tannery's unhairing processes.

The study was practical in nature with data taken on a full production scale unit capable of recovering all of the sulfides from a 5,000 hides-per-day-tannery. The advantages of the large-scale testing was the elimination of scale-up problems for future units. The disadvantage of the approach is that the system was part of the entire operational scheme of the plant and variables were required to be kept to a few operating limits.

The Blueside Company is the first tannery of its type in this country. This tannery produces only leather in the "blue" state. Cattlehides are put through the unhairing process and chrome tanned as wet blue hides. The chrome tanned hides are shipped to other tanneries for further wet and dry processing into finished leathers.

The sulfide reclamation unit is also a "first" and was constructed at the same time the tannery was built. The tannery grew from a starting production of 5,000 hides per week to its present production of over 25,000 hides per week. Concurrently to this growth, the sulfide recovery unit was being operated, modified and improved

The project goal to demonstrate a practical plant-scale method of removal and recovery of sulfides from a tannery waste stream was accomplished.

ABSTRACT

A full scale sulfide reclamation plant was constructed to demonstrate the feasibility of removing and recovering for reuse the sulfides in the wastewater of a large cattlehide tannery producing 25,000 hides per week.

The combined tannery effluent from the soaking, unhairing, bate, pickle, and chrome tanning wastes is screened and clarified. The clarified effluent is pumped on a continuous basis to a degasifier in which acidification to a pH 5.0 - 5.5 using sulfuric acid is effected. The hydrogen sulfide liberated from the wastewater is carried by air stream to an absorption tower where is is absorbed in recirculating caustic soda until a desired sodium sulfide concentration is achieved. The sodium sulfide is then reused in the tannery's unhairing process.

Quantitative removal and recovery of the sulfides is accomplished. The sulfide reclamation plant is operational seven days a week.

The sulfide reclamation economics indicate a savings in material and freight costs of approximately $92,052 per year or $84.84 per 1,000 hides.

An additional benefit resulting from the acidification of the total tannery wastewater is the coagulation of the solubilized proteins which could be removed by secondary sedimentation. Their removal will result in a sizeable reduction of the pollution load and the related sewer surcharge.

This report is submitted in fulfillment of Grant No. 12120 EPC by Blueside Company, Inc., under the partial sponsorship of the U.S. Environmental Protection Agency. This report covers a period from March 1970 to April 1976, and work was completed as of April 1976.

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ACKNOWLEDGMENT

This project was conducted by a number of people over its terms of activity. The original project was negotiated by Lee R. Lyon of Blueside Real Estate, Inc., Dr. Robert Culver of Camp, Dresser, and McKee Consulting Engineers did the preliminary technical work on the project including the designs and specifications of the equipment. Dr. Culver was also the consultant on the project during the initial phases of the work.

Mr. Ronald Collins, of Blueside Real Estate, Inc., conducted the early studies in the project. The project was completed by Robert H. Sayers and Roger J. Langlais.

Dr. Thomas Thorstensen, of Thorstensen Laboratory, was consultant in the final phase of the project.

Mrs. Bea Porter, an executive secretary at Blueside Company, graciously performed the typing and associated tasks required in the preparation of this report.

This project was supported by the U. S. Environmental Protection Agency and its agency predecessors through Research and Demonstration Grant No. 12120 EPC.

The support, encouragement, advice, and patience of the Project Officer, W. L. Banks, is greatfully acknowledged.

SECTION 1

INTRODUCTION

The largest segment of the leather tanning industry in the United States is the tannage of cattlehides. Cattlehides are primarily produced in meat packing areas in the midwest. Hides are salt cured and shipped to the leather tanning sites at east, midwest, and west coast locations. There is a trend to locate tanneries in the area near the source of the hides for freight economies.

Traditionally, hides have been cured near the slaughter house, shipped to tanneries at varied locations, tanned to the blue, retanned, and finished into leather at the single location. Costs to ship cured hides is more than double the cost of shipping partially tanned hides; i.e., chrome tanned blue stock. New tanneries located near the source of the hides can effect these savings and move pollution loadings from the older tannery sites.

The Blueside Company's tanning operation at St. Joseph, Missouri, is one of the first of a new type of tannery. The Blueside Company receives both fresh and cured hides from packing plants. These are then given treatments of soaking, fleshing, unhairing, bating, pickling, and chrome tannage. Chrome tanned leather is then wrung, palletized, and shipped as "leather in the blue" to other factories for further processing into finished leather.

The tanning of leather results in very high pollution loading particularly from the beamhouse operation (soaking and unhairing). In the study of the leather industry (1) made under the Environmental Protection Agency for the purpose of determining the nature of tannery wastes, it was reported that there were approximately two hundred tanneries in the United States processing approximately nineteen million cattlehides per year.

Industry data of wastewater from these tanneries, prior to treatment, indicated that the wastes contain approximately 8.5 pounds of sulfide as well as 95 pounds of BOD and 140 pounds of suspended solids per 1,000 pounds of hides processed. The quantity of sulfide discharged in the waste stream, on the basis of nineteen million cattlehides per year processed through the unhairing, would be approximately eight million pounds. This sulfide in the tannery effluents is a source for recovery. (2, 3, 4) Sulfides are objectionable for direct discharge into waterways because of their toxicity to wildlife and aquatic organisms.

Sulfides consume oxygen in the stream. They can generate undesireable odors which become a public nuisance. Hydrogen sulfide gas generated in a sewer or in concentrations above 1,500 mg/m is a deadly poison. Hydrogen sulfide in sewers can cause corrosion of iron pipes, and decrease the efficiency of secondary treatment.

The removal of sulfide from the waste, prior to discharge, can be done by aeration in the secondary treatment. There is objection to using the sulfide oxidation by aeration in the secondary treatment since there is some loss of sulfide directly into the atmosphere. The sulfide in the aerator will consume some of the oxygen thus reduces the effectiveness of the secondary treatment.

Sulfide can also be removed by the oxidation of the sulfide to sulfate by air using a manganese sulfate catalyst. In this system, the sulfide bearing wastes are placed in a tank, manganese sulfate is added as the catalyst, and the wastes are aerated for four to six hours. This system is conducted on a batch basis. It is costly in terms of power and can not be adapted to a continuous process as is the system that is used at The Blueside Company. (5, 6, 7, 8, 9)

In the Blueside system, the sulfide is removed by acidification of the wastes to form hydrogen sulfide. Hydrogen sulfide with its limited solubility at the low pH is then removed by an air stream.

The air stream is then conveyed to a gas scrubber within which sodium hydroxide is recirculated. The sodium hydroxide reacts with the hydrogen sulfide to form a solution of sodium sulfide in the sodium hydroxide which can be reused in the tannery processes.

The objectives of this demonstration grant was to determine the operating characteristics and economics of the wastewater treatment system and the sulfide removal-recovery system.

A study was conducted on the full flow of wastes from the tannery. Small scale laboratory studies on the recovery of wastes are known not to provide a representation of plant conditions. The engineering of the equipment and the effectiveness of the present design is of prime importance.

The chemistry of sulfide removal-recovery system is well understood. A discussion is presented in the Appendix.

Outside the scope of this project, but initiated by the interest created by the project, the Blueside Company undertook two additional studies. The company investigated the feasibility of secondary sedimentation of the coagulated protein resulting from the acidification of their effluent during the sulfide removal. Secondary sedimentation would further reduce sewer surcharges on BOD_5 and solids discharged. The feasibility of a system for chrome recovery and reuse was also investigated.

All data presented uses English units of measurements except for laboratory data. This follows industry practice.

SECTION 2

CONCLUSIONS

This project has shown that the sulfides from the sulfide bearing wastewater of a large cattlehide tannery can be reclaimed for reuse in the tannery's unhairing process. The system produces a commercially acceptable grade of sodium sulfide in caustic soda at a 15% sodium sulfide concentration with a residual 2% caustic soda.

The results of this investigation show that the sulfide is completely removed from the wastewater by acidification to a 5.0-5.5 p H. The recovery rate from the wastewater is approximately 98%.

With adequate acidification of the sulfide bearing wastewater, complete removal of the sulfides is assured and expensive chlorination or oxidation of residual sulfide is not necessary.

The design expectations of the sulfide reclamation have been exceeded. The system has satisfactorily allowed the recovery of sulfide from tannery wastewater containing 1,400 mg/l of sulfides.

The operational characteristics of the system as related to liquid and vapor flows have been established to ensure a safe operation.

Three design problems with the sulfide system remain to be solved. First, the air diffusers in the degasifier trays become clogged with proteins that precipitate during acidification causing downtime for cleaning every fifteen days for a twelve hour period. Second, the air blower should be changed to include a variable drive, thereby, allowing greater control of the air flow which serves to dilute the hydrogen sulfide enroute to the absorber. At lower influent flows, a lower air volume is desirable. At higher influent flows, higher air flow to a maximum of 800 CFM is desirable. Control of air flow is needed to ensure that the hydrogen sulfide concentration enroute to the absorber remains below the lower explosion limit of 4% H_2S in air. Third, additional absorber capacity is required.

Economic evaluation shows that the sulfide recovery-reuse system was profitable. Total annual costs for the system's operation, maintenance, and depreciation of equipment at 1976 prices was $305,000. The annual saving in cost for sulfide chemicals was $397,000. The net saving amounted to $85 per 1,000 hides processed.

The sulfide recovery-reuse system reduced the discharge of sulfide to meet the municipal ordinance and the BOD_5 of the wastewater. These reductions in pollution loading decreased the municipal surcharges which are based on BOD_5, flow, and suspended solids discharged to the sewer.

Secondary sedimentation of the coagulated proteins, resulting from the acidification necessary for sulfide reclamation, will result in approximately 80% reduction of the suspended solids, and 60% of reduction of the BOD_5 pollution loadings. These reductions would effect an estimated economy of $87,000 in sewer surcharges. Chrome reclamation and reuse indicate an estimated economy of $150,000. Once these systems are on stream, their economies would reduce the total wastewater treatment cost at Blueside Company to an annual operating cost of $120,271 based on 350 days per year. At 21,700 hides per week, the total wastewater treatment cost will equate to $95/1,000 hides processed.

SECTION 3

RECOMMENDATIONS

In order to minimize solids carry over into the degasifier, additional emphasis must be placed on the clarifier to ensure that short-circuiting of clarifier flows for proper settling of solids does not occur. The influent flow into the clarifier center should be baffled below the outflow to spread out the flow causing the inflow to the basin to be more quiescent and better distributed for its downward flow into the settling zone. (12) Continuous grease skimming and removal should be maintained to keep the clarifier surface clean. Turbine speed should be adjusted to a speed which will allow quiescent mixing of the inflow. Sludge removal from the bottom of the clarifier should be controlled so that sludge depth is maintained below 20 inches at all times ensuring sufficient depth space above the sludge level for settleability of solids. A float activating switch should be installed in the rim to signal the sulfide reclamation system operator that the upper and lower levels of wastewater available for the sulfide system have been reached.

Operation of the sulfide reclamation system has been manual rather than automated through most of the investigations required in the project studies. Automation should be refurbished and simplified. Sensing pH electrodes should be installed in the top tray of the degasifier and in the overflow tower. A recording controller would not only provide a record of the pH during the operation but control the acid feed pump running time maintaining acidification within the high/low of 5.5 - 5.0 pH. The sensing electrode in the top tray would be a flow through type to prevent clogging. The sensing electrode in the overflow tower would be an immersion type and would record the pH of the degasifier effluent to the city sewer line. The high-low limit controlling relay for this electrode would sound an alarm if the pH was out of range. While it is recognized that the degasifier influent averages to pH 8.5, a change in the flow rate in order to maintain continuous operation of the system currently requires a manual change of the acid feed pump.

A variable drive air blower having air displacement capability in the 100 to 800 cfm range should be installed as a replacement of the 1,000 cfm blower in use. If the current blower is retained, it should have a 3 inch valve outlet installed at a point prior to entry into the plenum at the base of the degasifier. Opening or closing of this valve would allow the operator to adjust the rate of air flow into the degasifier at the necessary level required for the sulfide content being reclaimed.

In the system as studied the concentration of the caustic soda was limited to 10% to prevent the formation of sodium sulfide solution in excess of 15%. Facilities should be winterized to allow the use of 25% caustic soda. The incorporation of a second absorber of the present type installed in series with the first would allow the formation of sodium sulfhydrate which is not subjected to as low freezing points as sodium sulfide. The method would involve the use of two absorber towers in series. The exit gas stream from the first tower would be passed to the bottom of the second tower. Initially, both towers would be filled with caustic soda solution. Hydrogen sulfide would be passed to the first tower, forming Na_2S first and then NaSH. As the production of NaSH nears completion, the H_2S that is not consumed would be passed to the second tower, forming Na_2S in that tower. Once the NaSH was formed in the first recirculating tank, the H_2S flow from the degasifier would be passed from the degasifier to the second tower to complete the formation of Na_2S and subsequently NaSH. Meanwhile the NaSH in the first tower would be replaced with fresh caustic soda solution. The gas stream from the second tower would then be passed to the first tower. This process of alternating absorber towers for the production of NaSH would be repeated. A system of this type would eliminate flue emission in the current sulfide reclamation system.

Future systems should consider a lower liquid level in the degasifier tray and possibly the use of valve type trays as designed by Koch Engineering Company. The valve type trays consist of perforated decks on which round movable caps are mounted. The caps which operate like check valves are approximately 2 inches in diameter and have a limited lift which is accomplished either by a hold-down cage or by integral guide legs and lift stops. The valves are made in different metal gauges and are normally installed in alternating rows of light and heavy valves, parallel to the outlet weir to provide good vapor distribution over a wide range of air flow rates. At lower air flow rates, the lighter valves are lifted to an open position. As the flow rate increases, the lighter weight and then the heavier weight valves open progressively wider to their full open position. Even at the lowest loadings, air would flow upward through the slightest crevice thus preventing any leakage and making tray gasketing unnecessary. Tray gasketing, however, is available. The possibility is that this valve tray type design using low liquid levels in each tray would eliminate the downtime for clean-up that is required in the present system. Low liquid levels in the trays with air flow mixing would keep solids in the wastewater in suspension during its flow through the degasifier. (16, 17) The number of trays required would be increased dependent on retention time required. The same type of tower of proper dimension and necessary trays could be used as an absorber. Fresh caustic soda would flow into the top tray of this unit and flow countercurrent to the H_2S/air vapor. The emergent solution at the bottom of the unit would move to tankage as sodium sulfhydrate or sodium sulfide solution in caustic soda dependent on the number of trays used.

For the present sulfide reclamation at Blueside Company, a second full set of check valve type air diffusers should be in stock for use as replacements when the tower is opened for cleaning. The downtime for the system would be reduced to 6 hours. The dirty diffusers taken from the tower would be cleaned during the interim period between tower clean-outs. The size of the drain-out pipe from each degasifier tray should be increased from 1½ inch I.D. to 3 inch I.D. The level of the drain pipe should be such that full drain out of the tray is possible. The present drain pipe outlet on each tray allows one inch residual of liquid in the trays and makes wash-out of solids difficult. With a large drain pipe and additional spray heads in the water line at the top of each tray section, spray washing of the tower would be safer for the operator.

Secondary sedimentation of the degasifier effluent is recommended for the removal of the coagulated proteins resulting from acidification of the tannery wastewater to 5.5 - 5.0 pH. The removal of these solids will reduce pollution loadings by 80% for suspended solids and 60% for BOD5 resulting in substantial economies in sewer surcharges.

The sulfide reclamation system is recommended for use in the treatment of sulfide bearing wastewaters. Waste stream segregation of the sulfide bearing wastes coupled with pretreatment to minimize solids is necessary. The sulfide system's useage reflects cost savings.

SECTION 4

HISTORY OF THE PROJECT

This project was designed by Camp, Dresser and McKee of Boston, Massachusetts and was proposed by The Blueside Company of St. Joseph, Missouri to the Federal Water Pollution Control Administration in 1970. A grant was awarded covering the design, construction, and operation of a sulfide recovery process to handle tannery waste. The plant was to be full scale, handling all waste from a major tannery.

Preliminary experiments in the laboratory demonstrated that sulfides were released from tannery waste when sulfuric acid was added. Air was passed through the mixture to drive the hydrogen sulfide out of the liquid media. The air H_2S mixture was then run into an absorber where the H_2S was converted to a sodium sulfide solution in a reaction with sodium hydroxide.

Laboratory trials using this principle of successive chemical reactions resulted in complete removal of the sulfide from the liquid and the absorption in sodium hydroxide solution. The resulting sodium sulfide solution was suited for unhairing reuse. Based on the laboratory tests a pilot plant was designed.

A pilot plant was first installed at the Prime Tanning Company, Berwick, Maine. Tests were conducted over a two week period during which the degree of acidification and various flow rates were tried. It soon became apparent that although acidification was releasing sulfide gas, it also was causing a precipitate to form. The precipitate was the result of lowering the isoelectric point of the proteins as the pH was changed from 12.0 to 5.0. The proposed design used a packed column in the aeration step it was anticipated that the proteins would soon plug the column.

The next modification tried was to use a diffusion technique by bubbling air through the acidified waste water. Through this work, rates were determined for complete sulfide release and for the appropriate air rate to scrub the sulfide out of the water. Calculations were made for scaling-up the pilot plant to a full production sized unit.

The degasifier section design was based on pilot scale work and an absorber was selected from commercially available

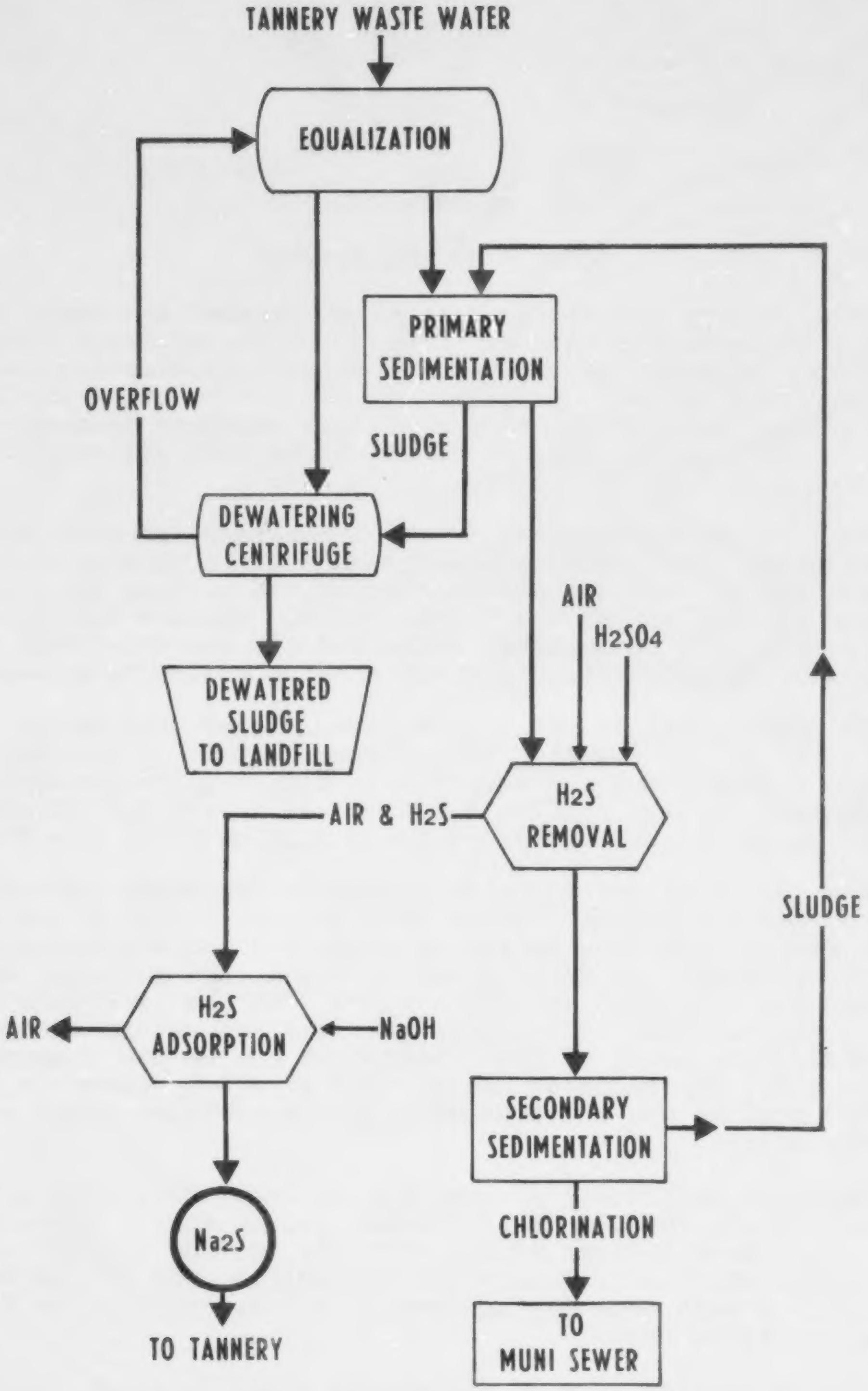

TANNERY WASTE WATER
EQUALIZATION
PRIMARY SEDIMENTATION
OVERFLOW
SLUDGE
DEWATERING CENTRIFUGE
DEWATERED SLUDGE TO LANDFILL
AIR
H_2SO_4
AIR & H_2S
H_2S REMOVAL
SLUDGE
H_2S ADSORPTION
AIR
NaOH
SECONDARY SEDIMENTATION
CHLORINATION
Na_2S
TO TANNERY
TO MUNI SEWER

Figure 1. Waste water treatment, original design.

equipment. The acififying degasifier section was of an original design and included diffuser caps on the trays to insure adequate mixing.

The operation of this equipment was first planned to follow the scheme illustrated by Figure No. 1. This involved a pretreatment step of equalization and settling before acidification. This would reduce the amount of solids in the acidification/degasifier section. The desire to remove all the available sulfide would not permit separation at the first step in the process.

The alternate sequence adopted was to first mix in a wet well, equalize and clarify in the next step. The clarified supernatant was then sent to the degasifier. The sludge was to be sent to a landfill. The resulting design is illustrated in Figures No. 2 and 3.

The first plant runs of the sulfide reclamation system proved to be frought with many problems and difficulties. Solids build-up occurred around the diffuser caps and at the bottom of the overflow drain. Flooding, carry-over of liquid into the absorber and general imbalance of the hydraulics in the towers also occurred.

The original construction was lacking ancillary units by which to measure air flow, sample the air or liquid during a run and to adequately control the process.

It had been recognized that the solids could increase during the processing and bubble caps were judged necessary to insure mixing. Solids deposition occurred on each level of the degasifier and at the drain from the outer shell during the first series of runs.

The acid mixing zone was on the top tray and the gas exited at the side. The rate of air/gas flow caused material to be entrained from the top of the tower into the absorber. This caused chrome to reach the circulating caustic along with other waste water and reduced the effectiveness of the absorption.

The carryover defect was not immediately apparent because of seemingly normal operation for few hours each day. The back pressure in the blower would increase from 6.5 - 7.5 psig to a flooding range of 9 - 10 psig. The progressive increase in pressure would allow only a few hours of operation before there was a need to clean out the unit. It was during a cleaning session that the carryover was identified.

The correction of the poorly located gas outlet pipe was attempted by adding a sock filter in the piping to the absorber. Although the sock removed material in excess of 1 micron in

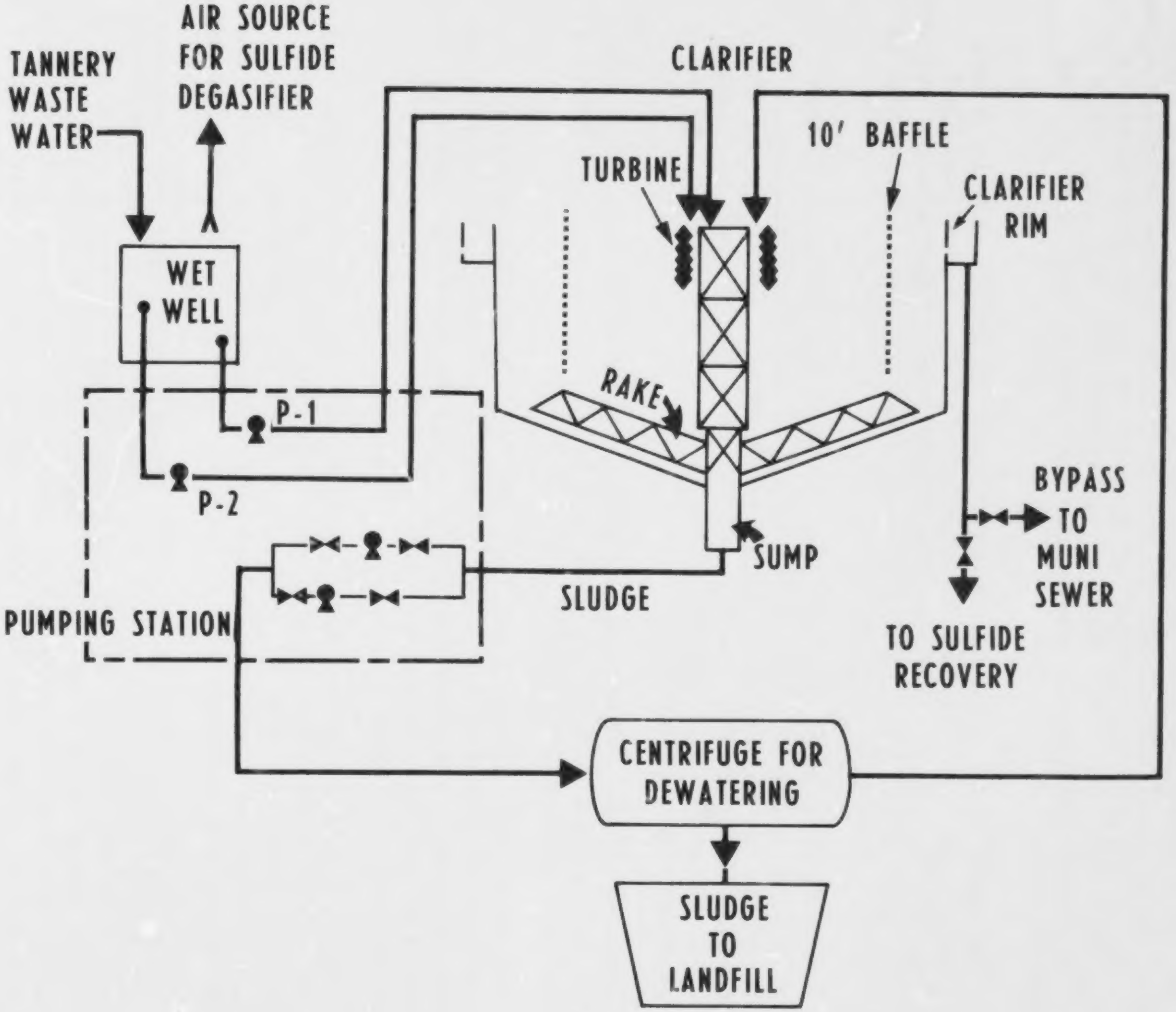

TANNERY WASTE WATER
AIR SOURCE FOR SULFIDE DEGASIFIER
WET WELL
P-1
P-2
PUMPING STATION
CLARIFIER
TURBINE
10′ BAFFLE
CLARIFIER RIM
RAKE
SUMP
SLUDGE
BYPASS TO MUNI SEWER
TO SULFIDE RECOVERY
CENTRIFUGE FOR DEWATERING
SLUDGE TO LANDFILL

Figure 2. Waste water treatment, as constructed (1970).

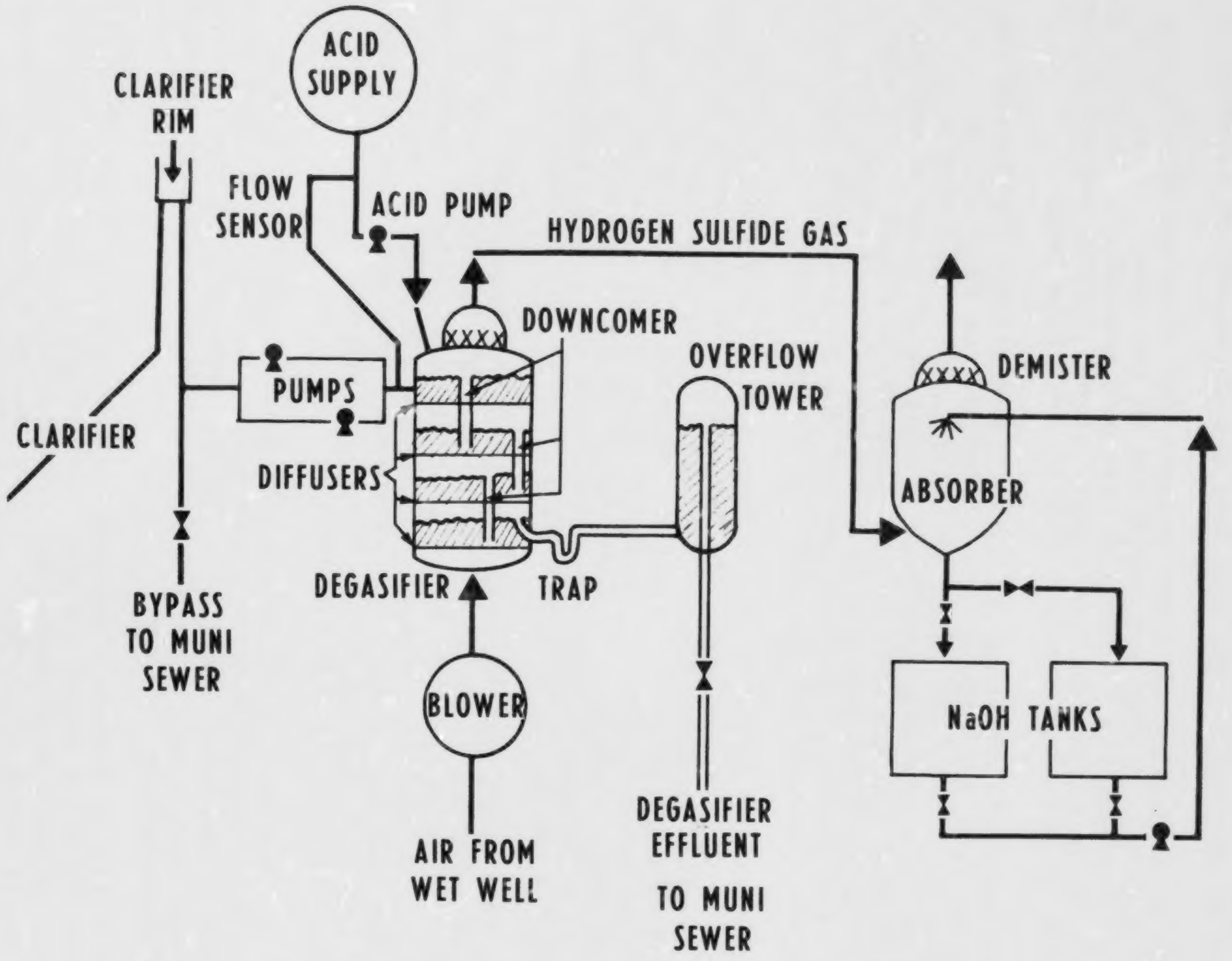

CLARIFIER
RIM
ACID
SUPPLY
FLOW
SENSOR
ACID PUMP
HYDROGEN SULFIDE GAS
DOWNCOMER
OVERFLOW
TOWER
DEMISTER
PUMPS
CLARIFIER
DIFFUSERS
ABSORBER
DEGASIFIER
TRAP
BYPASS
TO MUNI
SEWER
BLOWER
NaOH TANKS
AIR FROM
WET WELL
DEGASIFIER
EFFLUENT
TO MUNI
SEWER

Figure 3. Sulfide reclamation system.

diameter, the installation was difficult to maintain requiring frequent cleanout and replacement.

Data on air flow was non-existant in early experiments and with certain assumptions made, was labeled as 700 cfm. Later work was to determine that the flow was in excess of 1,000 cfm.

The installation of sight glasses and pressure gauges gave further insight to what was occurring in the tower. With these and other corrections it was then assumed possible to monitor the process. Flow rates, filling times, liquid levels and pressures could now be obtained and more significant runs made.

The unit was modified to correct entrainment by moving the gas outlet from the side to the center of the roof of the degasifier. A two foot diameter column, four feet high was installed as a demister section. A grating of plastic modules were included for gas diffusion. This was followed by a water spray of about five gpm, eighteen inches above the diffusion layer. A six inch thick demister pad was placed above the spray section and just before the exit to the gas line.

An U-shaped pipeline connection between the bottom level downcomer pipe and the overflow was installed to insure adequate water pressure between the degasifier and the absorber at the moment the air blower was started. Without this balancing, the air stream would follow the path of least resistance and create difficulties. Proper operation, based on experimentation, called for turning on the air blower when the lower sight glass indicated a depth of 46 inches of liquid in the vessel.

A gate valve was installed between the degasifier and the overflow tower to allow stand-by operation with the blower on. The degasifier would then be full of effluent with effluent pumps off and acid addition stopped. This was the mode of operation used when effluent supply was exhausted. The operation of the blower kept the diffuser caps from clogging and saved filling time when processing was resumed.

A different type of bubble cap was designed utilizing a flat sheet of neoprene with cross slits and held by a half union. This was to minimize clogging. Trials were made in the top tray, and while it did not clog, the neoprene flaps were soon distorted and allowed severe leakage.

The diffuser design has not been solved since the unit still requires cleaning every ten to fifteen days. This maintenance consumes about twelve man-hours. The location of diffusers immediately below the downcomer pipe caused bypassing of the air. This in turn restricted the effluent flow and contributed to the overflow condition. Selected diffusers were plugged and this problem was reduced.

A vent consisting of a two inch opening was installed to allow trapped air to escape. This also aided in the correcting of the overflow condition.

Imbalance existed in the absorber and caused flooding to a height of sixteen inches above the caustic return line. The flooding caused heavy misting of the caustic solution into the tower flue. Examination disclosed that the plastic packing was in complete disarray and the lower support grating out of place. The movement of the packing into the recirculation line caused a partial blockage. The condition may have existed from the first day of installation or could have been caused by severe flooding.

Repacking of the absorber solved the flooding problem. In addition, the caustic spray manifold had been installed so as to aim at the demister pad. When this was turned downward the caustic flow into the flue ceased. At the same time the high air flow rate, 1,000 cfm, had contributed to carrying large droplets into the stack. The lower flow rates tried further reduced the carryover.

The unit was installed out of doors with no winterizing. This resulted in frozen pipes, broken fittings and the unheated caustic/sulfide solutions solidified to cause blockage. Sludge build-up in pumps whenever they were stopped without flushing hampered the systems operation. Corrosion in the solenoid valves, automatic console components and electrical short circuits caused excessive maintenance and consumed time. As each repair was made a solution was tried which eventually reduced these bottlenecks to a reasonable level. Insulation, heating of solutions and tracing of lines with steam solved many of the defects.

The original system specification called for the use of 10% caustic soda in the recirculating tanks in order to form a 15% sodium sulfide solution suitable for re-cycling as an unhairing liquor. The low concentrations were necessary because of freezing characteristic of the solutions. An 8% to 12% sodium sulfide solution will freeze at 15°F as will a 10% caustic soda solution. Higher concentrations freeze at higher temperatures and make pumping difficult. The addition of heated lines, tanks and lines would allow higher caustic concentrations and minimize flue gas emissions.

When the Blueside plant first started the use of the sulfide recovery system, the production ranged between 5,000 to 10,000 hides a week. The effluent contained between 200 to 400 ppm of sulfide. The increase to 20,000 plus hides a week raised the sulfide content of the effluent to over 1,300 ppm.

Corrosion was one of the major deterrents to progress in the sulfide recovery system. The center column of the degasifier supporting the bubbler cap trays was found to experience corrosion at the welds. Seams required re-welding and cementing to prevent further corrosion. The black iron sulfuric acid line required replacement on two separate occasions. A check valve arrangement should eliminate clogging and syphoning during intermittent running. If dilute waste acid becomes available then a polypropylene acid resistant piping would be required.

The acid proportioning pump experienced a broken elastomeric diaphram on numerous occasions. Replacement of the diaphragm provided no relief and a pump replacement presented the same problem.

A rubber expansion boot between the air blower and its muffler hardened with age and broke apart. Condensation in the muffler caused corrosion and air leaks. The sound level at 1,000 cfm measured 95 decibels and required ear protection. Lower air velocities were accommodated without ear protection.

The first plans called for a centrifuge to be used to concentrate 8% solids from the bottom of the clarifier. This was a poor choice and was soon discarded. The 15% level could not be obtained as this was the lowest acceptable in a landfill.

The clarifier in turn was found unable to cope with the heavy solids load. No baffle was provided at the center which would direct the solids in a downward direction. There was no skimmer to remove grease and soap scum.

With all of the system difficulties, it became necessary to utilize the clarifier as a settling basin in order to produce the 15% solids concentration required by the landfill operator. This meant that a sludge depth of 24 - 36 inches was necessary to reach the 15% content. Companion to this difficulty, entrance roads at the only available landfill became impassable during winter months. The clarifier rakes were stopped and the sludge depth increased at the rate of 0.75 inches per 20,000 pounds of bluestock produced. The fact that no other contractor would take the sludge due to hauling distances and without adequate clarification, the evaluation of the sulfide reclamation came to a standstill during the winters of 1973/74 and 1975/76.

The pollution loading, generated by the processing of 20,000 hides per week, is comparatively very high. In order to stay in production, the clarifier was modified to pump the sludge out of the bottom of the basin to the clarifier rim. Here it was allowed to concentrate for manual removal. It was this ingenious arrangement that allowed production to continue as well as clarifier repair in 1974 and major plant modifications in 1975. The pretreatment and sulfide recovery system has been modified and expanded to avoid all the problems related in this history of the project. Other sections of this report detail the present system and explain how the problems of the past are now avoided.

SECTION 5

THE MANUFACTURING PROCESS AND POLLUTION LOADING

MANUFACTURING PROCESS

The Blueside Company in St. Joseph, Missouri, is a wholly owned subsidiary of Prime Tanning Company of Berwick, Maine. The Blueside Company is engaged in the manufacture of chrome tanned leather. The leather is not processed into finished leather; it is shipped to customers as chrome tanned hides (or sides) at an approximate 58% moisture content.

The leather produced is best identified by the term "leather in the wet blue state", or bluesides.

All hides are received pre-fleshed. The hides may be conventionally salted, brine cured or fresh (without salt cure). Fresh hides are processed immediately as received. Cured hides are processed as needed for production scheduling.

Process sequence is shown in Figure 4 and proceeds in the following order. All wet processing is conducted in hide processors of the cement mixer type.

RECEIVING: Hides are unloaded from rail-cars and trucks daily. Hide bundle ropes are removed and the hides counted as they are placed in pre-weighed numbered plastic coated "hide cans" affixed to pallets. When each hide can is full, it is re-weighed. Batch weights are made up in a staging area for loading into the soaking hide processors.

SOAKING: Hides are soaked in water containing a surfactant and alkali to allow rehydration to that state existing when the hides were first flayed from the animal. The soak waters, pH: 9.0, are drained upon unloading to the "common drain pit" into which all the tannery wastes flow within the plant.

FLESHING: As the hides are emptied from the soaker, they are individually clamped to a cable conveyor for transfer to a whole hide fleshing machine.

The fleshings are caught in a box and the water from the fleshing operation drains into the "common drain pit". The fleshings when drained are removed to landfill.

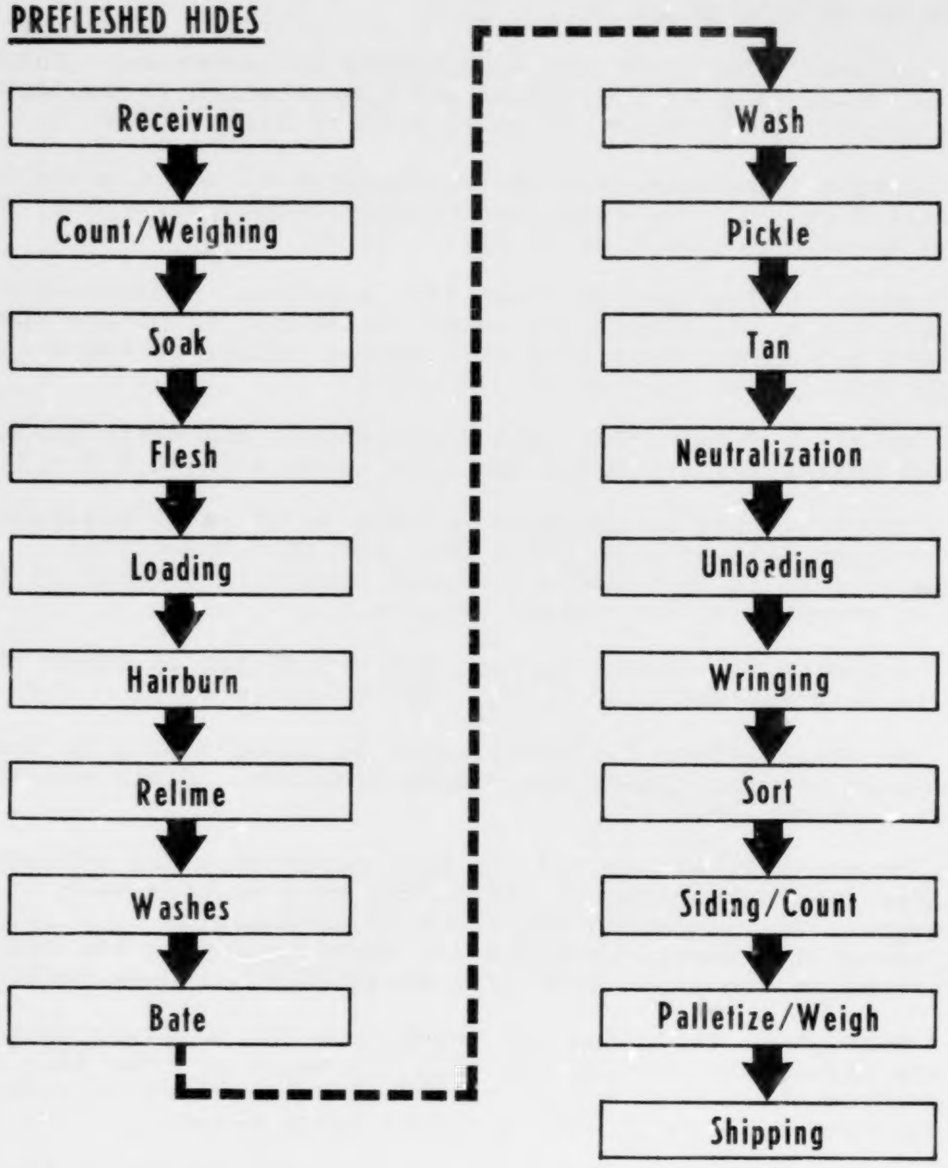

PREFLESHED HIDES
Receiving
Count/Weighing
Soak
Flesh
Loading
Hairburn
Relime
Washes
Bate
Wash
Pickle
Tan
Neutralization
Unloading
Wringing
Sort
Siding/Count
Palletize/Weigh
Shipping

Figure 4. Process flow diagram, Blueside Co.

HAIRBURN: The unhairing of the hide is conducted using a hair destruction system consisting of sulfide and lime. Drain solution is at a pH of 12.3 - 12.5.

RELIME: The hides are conditioned in limewater. Solubilizing of unwanted proteins, scud, and pigmentation is conducted in this cycle. Drain solution is at a pH of 12.3 - 12.4.

WASHES: Deliming and the elimination of waste products is conducted by batch washing for the most economical use of water. Drain solution is at a pH of 12.3 - 11.9.

BATE: Additional deliming salt solution, a pancreatic enzyme, and a surfactant are added to further eliminate unwanted protein and animal fats from the leather making collagen fibers. Drain solution is at a pH of 8.0 - 9.3.

WASH: A final water wash to eliminate the waste products of the bating cycle. Drain solution is at a pH of 8.0 - 9.3.

PICKLE: Salt is added to provide an 8° Baume solution of brine which will protect the hides from acid hydrolysis. Sulfuric acid is then added to lower the pH to a range of 1.8 - 2.0 in preparation for chrome tanning.

CHROME TAN: Sodium formate and chrome tan is added to the pickle solution and hide stock. The pH range's 2.8 - 3.2.

NEUTRALIZATION: An alkali salt is added slowly to increase the pH of the tan liquor for chrome fixation. Drain solution is at a pH of 3.8.

UNLOADING: As each of the hide processors are unloaded in turn, the chrome tanned hides drop onto an open mesh conveyor. The processed tan stock is transported to a large collection tub where the hides are spread out with the hide tail ends at the input side of a whole hide wringing machine.

WRINGING: The hides are wrung to a 58% moisture content. As the hides pass through the wringing machine, they fall onto a conveyor where they may be sorted as whole hides or allowed to be cut into sides by a siding rotary knife blade.

The chrome liquor from the wringing is drained to the "common drain pit".

PALLETIZING: Hides or sides are counted, folded and palletized. The pallets are covered with a plastic sheet. Pallets are weighed prior to shipping.

TABLE 1. TANNERY WASTEWATER AFTER SEDIMENTATION TO MUNICIPAL SEWER

WEEKLY PRODUCTION: 21,700 HIDES ***

PARAMETER	CONCENTRATION		
	Parts Per Million (p.p.m.)	Lbs./1,000 lbs. Hides	Lbs./Day
Flow	-	1500*	300,000*
BOD_5	4,800	60.0	12,010
Total Suspended Solids	5,020	62.8	12,560
COD	13,160	164.6	32,926
Oil & Grease	1,500	18.8	3,753
Chlorides	7,970	99.7	19,941
Sulfide	1,395	17.5	3,490
Sulfate	4,802	60.1	12,015
Total Nitrogen	1,350	16.9	3,378
Ammonia Nitrogen	600	7.5	1,501
Alkalinity	1,110	13.9	2,777
Total Solids As $CaCO_3$	26,783	335	67,012
Calcium	340	4.2	851
Cr_2O_3	350	4.4	876
pH	8.9**	-	-

* Gallons

** Standard Units

*** 60% Salt Cured Hides; 40% Fresh Hides

POLLUTION LOADING

The tannery operates 24 hours a day. Hide processors are loaded as they are emptied. As a result, the effluent is more steady in volume and composition than is usually found in tanneries. Normal production is 200,000 pounds of hides per day utilizing 300,000 gallons of water. The average discharge is 1,500 gallons per 1,000 pounds of hides at 208 gallons per minute.

The water used in housekeeping measures, domestic sewage, pollution processing, sewer flushing, and boiler blow-down is included in the 1,500 gallons per 1,000 pounds of hides.

A composite made from grab samples taken every 30 minutes over a 24 hour period was analyzed to indicate pollution loading remaining in the tannery wastewater after the clarifier. The samples were taken at the manhole to the city sewer. Table No. 1 lists the pollution parameter tested and the results obtained.

The sulfide reclamation system was not in use during the sampling period.

The municipal ordinance governing industrial wastewater pollution limits at St. Joseph, Missouri allows a maximum sulfide content of 10 parts per million to flow into the municipal primary treatment plant.

Evaluation of the tannery's process cycles identifies the distribution of sulfide bearing waste liquors in each batch of hides to be as in Table No. 2.

TABLE NO. 2

SULFIDE PRESENT AFTER EACH PROCESS CYCLE

Production Drain Sequence	Cycle Useage Waste Water Volume-gallons	Sulfide Present S=, ppm	Sulfide for Recovery, %
Hairburn	1,400	9,535	33.0
Chemical Relime	1,400	4,893	16.9
Water Relime	1,400	5,160	17.8
Wash	1,400	2,407	8.3
Wash	1,400	1,560	5.4
Wash	1,400	1,330	4.6
Bate	1,000	2,013	6.9
Bate Wash	1,400	1,000	3.5
Brine - Pickle	1,700	1,030	3.6
	12,500	28,928	100.0

The waste streams at Blueside Company are not segregated. All of the process cycles drain into a common pit which flows from the plant into a wet-well. This includes the pickle and chrome tan liquors when the hide processors (cement mixer type) are unloaded on completion of bluestock processing. The chrome tan liquors from the wringing operation also flow into the common drain pit. Soak liquors and housekeeping water requirements also flow to the same pit.

As this report is written, a chrome recovery and recycling system is in its second month of trials. During the course of studies for the sulfide reclamation system, all process cycle drains were into the common pit. With chrome recovery and recycle, the chrome tan liquors are handled separately.

The process cycles listed in Table No. 2 are all sulfide bearing. A lead acetate drop test on a hide at the end of the pickle cycle will indicate that the residual sulfide present at the start has been removed. The acidification of the pickle cycle converts the sulfide present to hydrogen sulfide. Each of the hide processors are vented to the atmosphere by roof top fans and the hydrogen sulfide is pulled from the mixer as it is formed.

TABLE No. 3

SLUDGE ANALYSES

LIQUID PORTION		SOLIDS PORTION	
PARAMETER	Parts per Million (ppm)	PARAMETER	Parts per Million (ppm)
Total Dissolved Solids	57,372		
Chemical Oxygen Demand	15,840	Chemical Oxygen Demand	241,600
Alkalinity as $CaCO_3$	5,000		
Chlorides	19,600		
Bicarbonate	3,944		
Carbonate	1,056		
Cr_2O_3	2.8	Chromium Cr_2O_3	12,500
Total Nitrogen	2,300	Total Nitrogen	31,400
Nitrates	Less than 0.01		
Calcium	300		
Sulfates	10,800		
Sodium	18,000		
Sulfide	Less than 0.01	Sulfide	80
pH	8.6*		

* Standard Unit

The sulfide bearing wastes total to 12,500 gallons per batch. Coupled with soaking liquors, boiler blowdown, chemical mixing water, and general housekeeping water useage; the amount of wastewater to be processed through the sulfide reclamation system amounts to 300,000 gallons/day.

The sulfide reclamation system provides the means for removing and recovering the sulfide from the total effluent on a continuous basis for reuse in process. The clarifier into which the plant effluent flows allows settleable solids to produce a sludge that must be removed on a daily basis to a sanitary landfill.

The settled solids form an 8% solids slurry in the bottom of the basin which is pumped to flow equalizing tanks. It is then pumped to filter presses for dewatering to a 50% solids content for removal to landfill.

The quantity of sludge at 50% solids to be removed daily amounts to approximately 43,000 pounds for 200,000 pounds of hides processed. Table No. 3 shows the analyses conducted on a composite sample of sludge representative of two days sluage removal. The pollutants and quantities shown indicate the effects of the settling in the clarifier. The sludge solids and its liquid portion show a total of 257,440 mg/l of COD present in the sludge whereas Table No. 1 shows that the clarifier effluent has 13,160 mg/l. The same beneficial reduction of quantities for other parameters is affected by sedimentation in the clarifier.

SECTION 6

WASTE STREAM PROCESSING

PRE-TREATMENT PRIOR TO SULFIDE RECOVERY

The effluent treatment system as first conceived at the initiation of this project is outlined in the flow chart, Figure No. 1.

The initial design was modified because of the belief that as Blueside Company's production increased during its formative years, wastewater technology would also advance. The advances in wastewater technology would, potentially, require the dismantling of antiquated equipment, thereby, increasing the costs of modifications. Essentially, it is cheaper and easier to add to a basic facility than to correct what appears to be a complete package. It was a wise decision based on the progressive changes that have been and are occurring in the tannery's effluent treatment system.

A basic treatment system, constructed in 1970, was in accord with the schematic diagram in Figures No. 2 and 3, and began operation in the mid-year of 1971.

The initial wastewater treatment starts out with the wet well into which the tannery wastewater flows and will vary chemically throughout the day. At some point in time, it will be alkaline to a pH of 12.5 and at other times, it will be acid to a 3.0 pH. The wet well is covered and is exhausted by being the source of air for the air-blower. Sulfide gases forming in the wet well are; therefore, drawn into the degasifier tower. Figure No. 5 is a photograph of the wet well.

Two pumps remove the wastewater collected in the wet well to the center of the clarifier. The pumps are electrically controlled by probe levels. At a given level, one pump is activated; at an increased level, when wastewater flow is higher, two pumps are operating.

As the wastewater flows into the center of the clarifier, it is caused to flow downward and toward the bottom of the basin by a rotating turbine. This downward flow assists in the settling of sludge solids. The downward flow is also outward toward the basin wall then upward to a point of outflow into the clarifier rim.

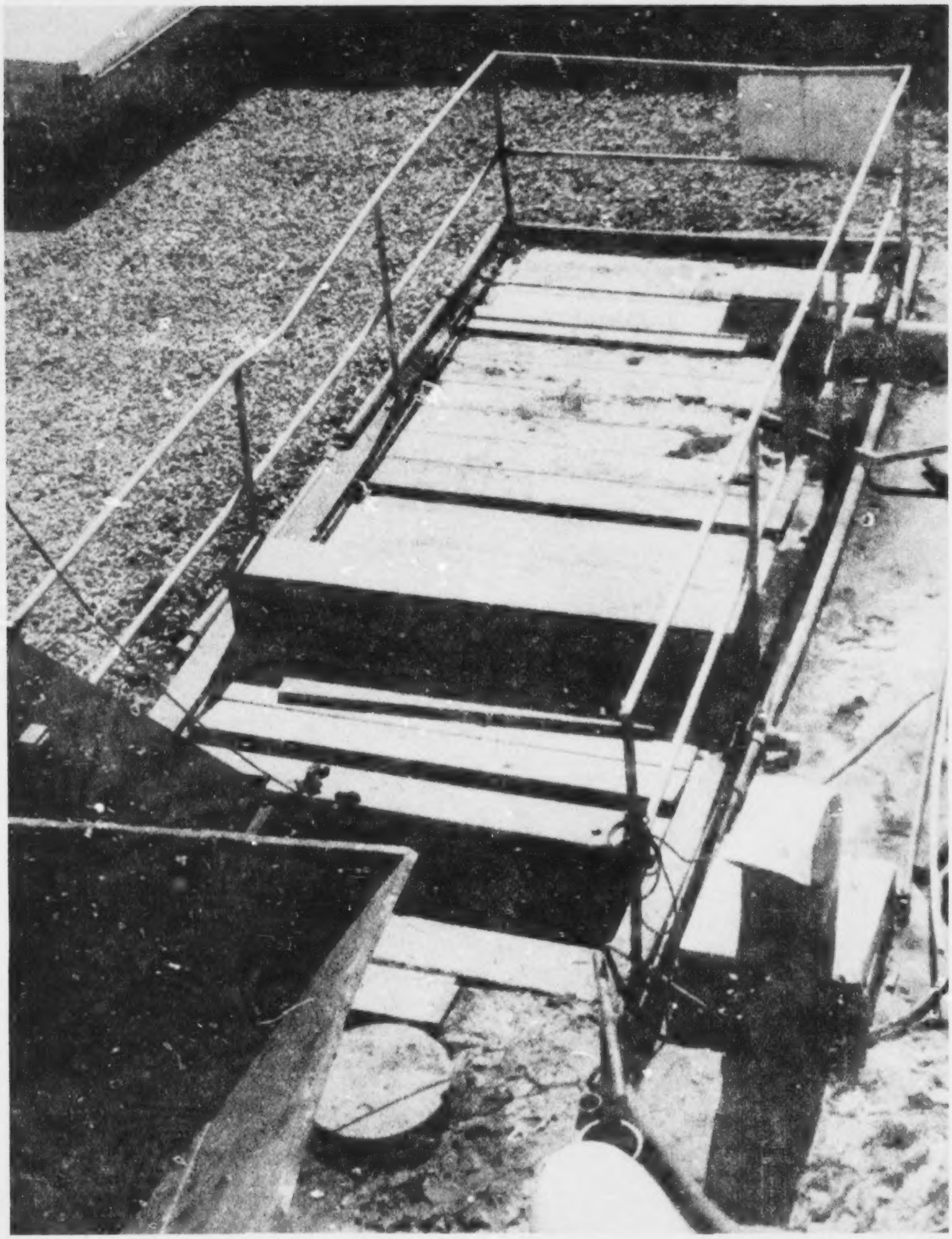


Figure 5. Wet well.

TABLE NO. 4

WASTEWATER TREATMENT SYSTEM EVALUATION, 1973

WEEKLY PRODUCTION: 16,200 HIDES

Parameter Unit: mg/l	Influent Composite	Effluent Composite	Percent Reduction
pH*	9.7	9.8	
BOD_5	9,133	5,123	43.9
COD	19,867	13,167	33.7
Settleable Solids	10,600	300	97.2
Total Solids	48,900	25,400	48.0
Suspended Solids	9,067	2,767	69.5
Sulfide	250**	264**	-
Alkalinity	2,896	2,660	8.1
Oil & Grease	570	21	96.3
Cr_2O_3	295	190	35.6
NH_3N	520	517	-
TKN	1,101	954	13.4
Total Phosphorus	40	20	50.0

* Standard Unit
**Sulfide Reclamation not operational

Pollution loading reductions of 43.9% in BOD_5, 33.7% in COD, 97% in Settleable Solids, 48% in Suspended Solids, 96.3%in Oil and Grease, 35.6% in Cr_2O_3, 13.4% in Kjeldahl Nitrogen, and 50% in Total Phosphorus are reflected in the test results.

The clarifier is 57 feet in diameter and has a normal depth of 16 feet. The capacity is approximately 340,000 gallons. The sludge collecting in the bottom is continually raked toward the center sump for removal to a dewatering system. A pumping station houses the effluent pumps which draw from the wet well, as well as the sludge pumps from the bottom sump to the dewatering step.

The clarifier is an essential part of the sulfide recovery system. It's purpose is to remove large solids which might interfere with the operation of the degasifier tower and to act as a reservoir to smooth out the fluctuations in flow and the quality of wastewater from the tannery. A more or less constant quality of wastewater can be pumped at a constant rate to the degasifier.

The liquid surface level of the clarifier is designed to fluctuate over a range of one foot six inches. The volume in this range is about 29,000 gallons or about 2.1 hours at the design rate of flow to the degasifier.

The clarifier rim weir separating the center from the rim (in the initial design) had one-half inch diameter holes every 18 inches all around the rim. The holes were positioned approximately 18 inches below the top of the rim weir. The liquid level was held at about six inches above the holes. If the level dropped to three inches above the holes, the pump (s) from the clarifier rim to the degasifier were throttled slightly. If the level rose more than twelve inches above the holes, the flow rate of the pumps was increased sufficiently to compensate for the higher liquid level. Adjustment of the flow rate was not frequent in the sulfide recovery runs.

Adjustment of the flow rate from the clarifier rim to the degasifier is kept to a minimum because each time the wastewater flow rate is adjusted, it is necessary to adjust the acid feed system to the degasifier.

Evaluation of the basic wastewater treatment system for its efficiency of reducing pollution loading was conducted in May, 1973. Composite samples of the influent to the clarifier as well as to the municipal sewer were averaged to yield the data shown in Table No. 4.

Grab samples of the tannery wastewater flowing into the wet well were taken every 30 minutes through a 24 hour period and composited. Grab samples were also taken of the clarifier effluent at the same time interval and composited.

For this evaluation, the sulfide reclamation system was non-operational.

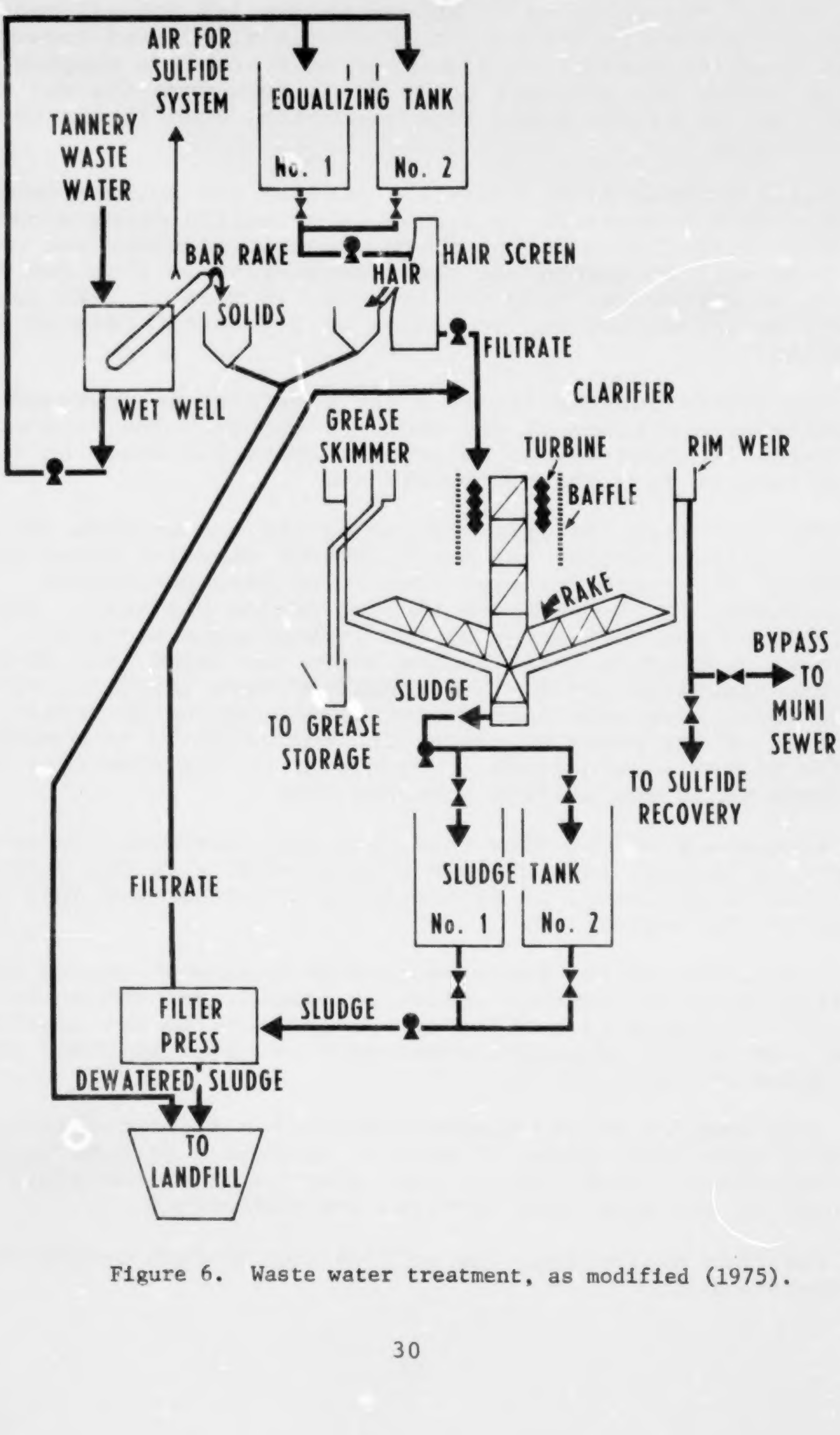

AIR FOR SULFIDE SYSTEM
EQUALIZING TANK
TANNERY WASTE WATER
No. 1
No. 2
BAR RAKE
HAIR SCREEN
HAIR
SOLIDS
FILTRATE
WET WELL
CLARIFIER
GREASE SKIMMER
TURBINE
RIM WEIR
BAFFLE
RAKE
BYPASS TO MUNI SEWER
SLUDGE
TO GREASE STORAGE
TO SULFIDE RECOVERY
SLUDGE TANK
No. 1
No. 2
FILTRATE
FILTER PRESS
SLUDGE
DEWATERED SLUDGE
TO LANDFILL

Figure 6. Waste water treatment, as modified (1975).

Three defects in the system's operation became apparent as the tannery's productivity increased; failure of the centrifuge to de-water, clarifier not settling and rake arm breakage and failure of internal baffling.

The centrifuge proved worthless as a means of dewatering the sludge generated in the clarifier. The centrifuge's inner cone wore out frequently requiring constant and costly repairs. Under the best operating conditions, the sludge concentrate produced was seldom dewatered to 15% solids and satisfactory for removal to landfill. The centrate returning to the basin was practically the same concentration as the sludge solids delivered to the dumpster for removal. It was necessary to allow water separation to occur in the dumpster and remove the water with a sump pump before the contractor would accept the sludge for disposal in the sanitary landfill.

The strength of the rake arm assembly in the basin proved inadequate to move the sludge collecting in the bottom of the basin to the center sump. The rakes became distorted resulting in a prolonged break-down.

Within three years, a 10 foot deep poly-vinyl baffle, initially installed peripherally within the clarifier, 10 feet in from the rim, became embrittled and crumbled. The purpose of this baffle was to insure a downward flow of the influent in its path to the clarifier rim. The downward flow is needed to enhance sedimentation of the settleable solids.

This baffle was rebuilt using steel plate. Two years later this baffle collapsed during a shut-down inspection. The inspection team, while pumping from the clarifier to lower the liquid level were not aware of the unequal pressures existing on both sides of the steel baffle. The sludge build-up was considerably higher on the outside of the baffle than in the center of the basin. When the liquid was lowered below the sludge level on the outside of the baffle, the pressure of the sludge against the bottom half of the baffle caused the baffle to collapse inward toward the center. This indicated that a great deal of sludge settling was occurring beyond the baffle. Stress increased on the ends of the rake arms in the absence of a proper sludge removal to landfill operation and contributed to baffle and rake failure.

A major redesigning and expansion of the wastewater treatment system was made in 1975. The schematic diagram, Figure No. 6, illustrates the current process. Sufficient flexibility in the piping and design lay-out of this system has been incorporated to allow other planned improvements to be incorporated.

TABLE NO. 5

WASTEWATER TREATMENT SYSTEM EVALUATION, 1976

(Pollution Loading Reductions of the 1973 system are from Table No. 4 - Weekly Production: 21,700 Hides)

Parameter Unit: mg/l	Influent Composite	Effluent Composite	Percent Reduction	
			(1976)	(1973)
pH *	8.8	8.7	-	
BOD_5	7,586	4,590	39.5	43.9
COD	20,286	8,485	58.2	33.7
Settleable Solids	7,676	3,250	57.7	97.2
Total Solids	36,282	27,644	23.8	48.0
Suspended Solids	7,675	3,256	57.6	69.5
Sulfide	915	930	-	-
Alkalinity	3,946	3,840	2.7	8.1
Oil & Grease	1,140	985	13.6	96.3
Cr_2O_3	242	150	38.0	35.6
NH_3N	540	532	-	-
TKN	1,395	850	39.1	13.4
Total Phosphorus		15	-	50.0
Phenol		13	-	
Chlorides	11,030	8,950	18.8	

*Standard Units

NOTE: Sampling accomplished when turbine not running, grease skimmer not operational, sulfide system not operational and hair screen operational.

Innovations built into the clarifier included increasing the slope at the bottom to provide easier flow of the sludge to the center sump. The rakes were reinforced and rebuilt into a tri-fork, i.e., three rake branches instead of two. Shear strips were installed in the rake drive mechanism. These shear strips are gauged to break under known torque, thereby, preventing distortion of the rakes under major stress. A baffle was installed immediately peripheral to the center turbine to allow direct downward flow for the settleable solids and provide strength to the baffle structure. A grease trap was installed from the liquid surface through the clarifier wall. A grease skimmer was installed on the rake arm ends to cause greases and fats floating on the liquid surface to be pushed into the grease trap.

Wastewater flow after the 1975 modifications as shown in Figure No. 6, still flows into the wet well. A bar rake screen, installed at the wet well, screens the wastewater for removal of fleshings and large particles of foreign matter (metal, plastic, etc.), these are collected in a dumpster for removal to a sanitary landfill.

The wastewater is then pumped to two 17,000 gallons equalization tanks in a new pollution treatment building. From these tanks, the wastewater is pumped through nozzles to impact on a hair screen (.020" gauge mesh) to remove the pulped hair residue. The hair free wastewater is then pumped into the equalization sedimentation clarifier where settleable solids form sludge in the bottom.

The sludge from the bottom is pumped into two 17,000 gallons holding tanks in the pollution treatment building. The sludge is then pumped into one of two filter presses which de-water the sludge to a 50 - 60% solids concentration for removal to sanitary landfill. The liquid removed from the sludge is pumped to the clarifier.

The new system was evaluated for its efficiency in reducing the tannery's pollution loading in September 1976. Composite samples of the influent to the wet well and to the municipal sewer were analyzed to yield the data presented in Table No. 5.

The composite of the influent consisted of mixing grab samples of the tannery wastewater taken at the wet well every 30 minutes for a twenty-four hour period. The effluent composite consisted of taking grab samples at the manhole to the municipal sewer at the same time intervals as that of the sampling at the wet well. At the time of sampling, the turbine in the clarifier, the grease skimmer, and the sulfide reclamation system were non-operational, the hair screen was in use.

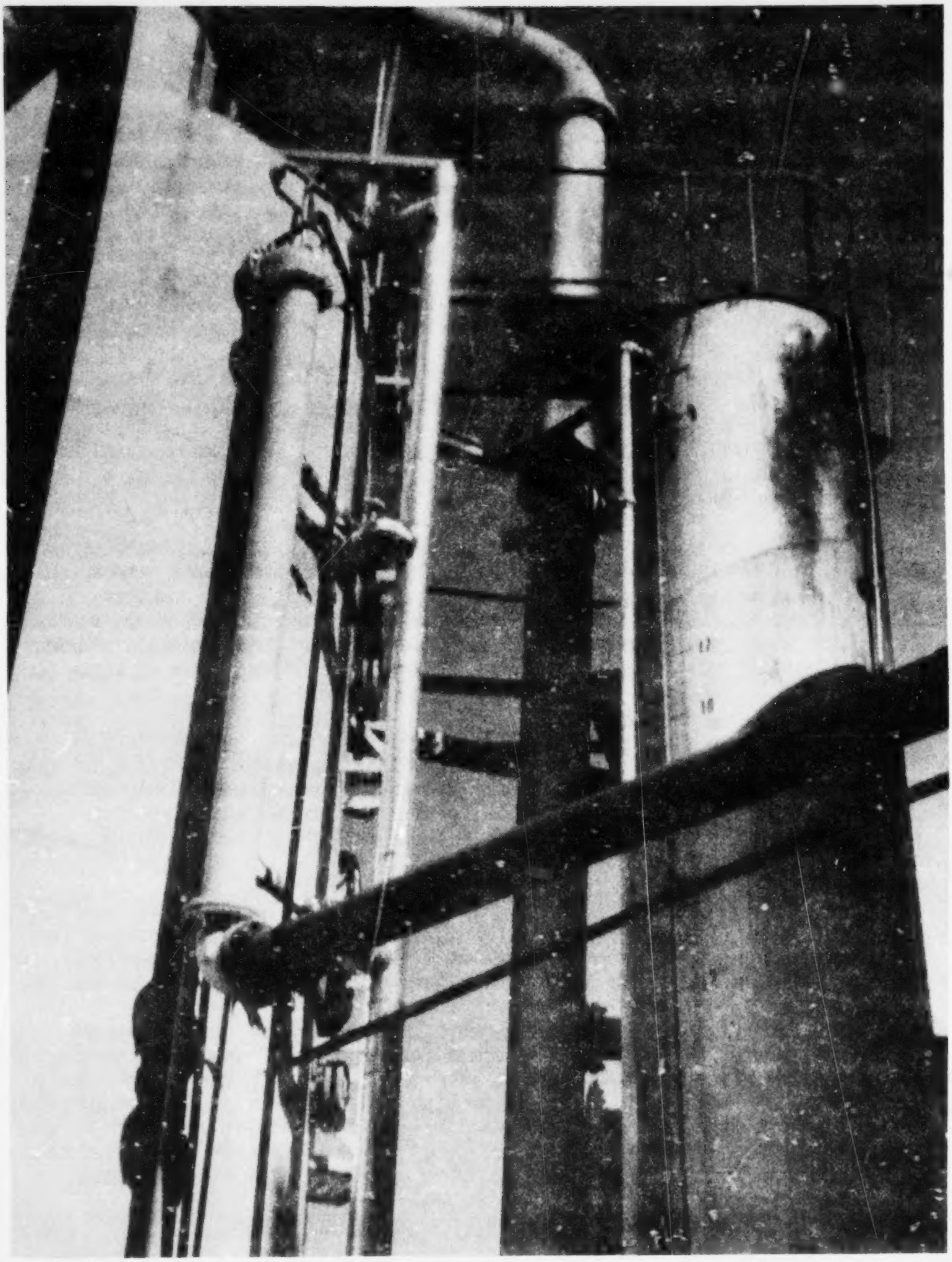


Figure 7. Degasifier and absorber towers.

Tannery process changes, occurring between May of 1973 and the 1976 wastewater treatment system evaluation, involved reduction in the use of lime in the hairburn and relime process cycles plus a reduction in the use of ammonium sulfate in the delime cycles and reductions in the use of pickle acid and chrome tan. Tannery productivity during the same period increased from 16,200 hides per week to 21,700 hides per week. Water conservation measures affected during this period resulted in total water useage of 300,000 gallons per day and remained relatively stable.

Comparison of the influent composites for the two evaluation periods revealed that the pollution loading in 1976 had 16.9% less BOD_5, 2.1% more COD, 27.5% less Settleable Solids, 25.8% less Total Solids, 15.3% less Suspended Solids, 266% more Sulfide, 100% more Oil and Grease, 17.9% less Cr_2O_3, 3.8% more Ammonia Nitrogen, and 26.7% more Kjeldahl Nitrogen, as related to a 33.9% increase in tannery productivity.

The percent efficiency of reduction comparison, between the 1973 and 1976 wastewater treatment systems, shows that the 1976 system has 4.4% less reduction capability in BOD_5, 39.5% less reduction in Settleable Solids, and 82.7% less reduction in Oil and Grease. These lower efficiencies are related to the non-operational turbine and grease skimmer.

It should be noted that the 1976 effluent composite contained 10.4% less BOD_5, 983% more Settleable Solids, 17.5% more Suspended Solids, and 4590% more Oil and Grease than the 1973 sample. The 1976 wastewater treatment system showed improved efficiencies of reduction by removing 24.5% more COD, and 25.7% more Kjeldahl Nitrogen. This benefit is related to hair removal by screening.

WASTEWATER TREATMENT THROUGH THE SULFIDE RECOVERY SYSTEM

As with the initial wastewater treatment system, wastewater from the clarifier rim is pumped to the sulfide reclamation system; i.e., to the degasifier.

The pumps to the degasifier are located in the chemical control area of the tannery adjacent to the automation console. The sulfide recovery system can be controlled from this point. The sulfide recovery system is schematically outlined in Figure No. 3. The degasifier is shown on the left in Figure No. 7 and the absorber on the right.

The degasifier tower has two functions, acidification and air stripping of hydrogen sulfide gas released from the acidified tannery wastewater. Sulfuric acid is added to the wastewater until 5.0 and 5.5 pH is reached.

The degasifier tower consists of four trays, each 6 feet deep, and 10 feet in diameter. The trays are placed on top of each other to form the tower. The trays are connected to each other by 80 air diffusers in the bottom of each tray and a 12 inch diameter downcomer for the liquid. The liquid is pumped into the top tray and flows downward and out of the bottom tray. Air is blown into a two foot high plenum under the bottom tray and bubbles up through each tray and exists at the top through a scrubber and mist eliminator. The liquid depth in each tray is maintained at 39 inches by the overflow level of the downcomer.

The liquid volume in each tray is normally 1,915 gallons, or 7,660 gallons total in the tower. At design capacity of 230 gpm, the flow through time is about 33 minutes. The design air flow is 700 cfm.

Air pressure is maintained in the tower by a liquid trap formed by the overflow tower. The overflow tower consists of an outer shell four feet in diameter and an inner overflow outlet pipe 10 inches in diameter, with a seven inch diameter adjustable overflow section. The adjustable overflow pipe can be set from a maximum height of 15 feet 11 inches to a minimum of 11 feet 11 inches above the overflow level of the lowest downcomer in the degasifier tower. Liquid flow is from the top tray where acidification occurs, downward through the tower and countercurrent to air flow through each downcomer in the degasifying tower into the outer shell of the overflow tower and then down the inner outlet pipe to the sewer.

The gas exit from the degasifier tower is from the top center of the tower through a three foot diameter scrubber and demister. The scrubber section consists of a two foot deep bed of one inch diameter plastic shapes (Koch rings). Four nozzles located about 18 inches above the bed continuously spray the bed with about 5 gpm of fresh water to wash the exit gas free from entrained particles of solids or liquids. Located above the spray nozzles is a four inch thick pad of polypropylene fibers which serve to filter out any water droplets picked up from the spray system.

The demisted gas then passes to the adsorption tower.

The adsorption tower is a standard fume scrubber, Model 731.5 produced by the Heil Process Equipment Corporation. This scrubber is guaranteed to remove 99% of the H_2S from the gas stream if the air flow is limited to 700 cfm and the sodium hydroxide solution maintained above pH 10. The recirculation rate through the scrubber should be no greater than 20 gpm at a pressure of 20 psig. As the air flow is increased to 1,000 cfm, the adsorption capability will drop significantly to a range of 80 - 90%. Two solution tanks equipped with sensing probes allow the preparation of a known concentration of sodium hydroxide solution for use in circulation. Each tank, in turn, is allowed to circulate through the adsorption tower to a point of sulfide saturation. The saturation point is sensed by a continous sampling of the adsorption tower flue exhaust for the presence of H_2S gas. At the first emission of H_2S, an alarm sounds indicating that the solution tanks should be switched. The first tank, after analysis, is sent to storage and a fresh solution of caustic soda is routinely made up.

SECTION 7

EQUIPMENT DESIGN FACTORS

Basic design data for the degasifier and absorber towers requires knowledge of the liquid and vapor characteristics that will be present therein. The data required includes the following:

a. Flow rate per unit time
b. Density, lbs/ft^3
c. Pressure, psig
d. Temperature, $^{\circ}$F
e. Total wastewater volume to be treated daily
f. Corrosion resistance
g. pH conditions

The densities of liquid and vapor loadings are required at actual inside tower conditions of temperature and pressure. Design specifications for the sulfide reclamation system were 230 gpm or less of liquid flow into the top tray of a four tray tower with each tray interconnected by a 12 inch diameter downcomer and 80 check valve type air diffusers per tray. Air was to be provided by a positive displacement blower at 700 cfm at a maximum of 10 psig into a plenum at the base of the tower. The liquid depth in each tray was specified at 39 inches. The downcomers were to be immersed deep enough into the liquid of the next tray so that air could not escape upward through them. Air was to flow upward through the air diffusers countercurrent to the liquid flow. The liquid was to leave the bottom tray and flow into an overflow tower having an adjustable outlet pipe for regulating liquid levels and pressures in the degasifier. The liquid would leave the overflow tower and flow to the city sewer. It was anticipated that the wastewater entering the tower would range in temperature from 50°F to 80°F. The liquid would have a maximum 1.2 specific gravity.

The mechanical requirements of the degasifier can be calculated from the specifications. The internal liquid and vapor loadings are required to ensure proper tray design.

The mechanical data requiring calculation include the following:

a. Wall and tray thicknesses
b. Tower cap
c. Manholes
d. Tray support rings
e. Downcomer
f. Vapor inlets and outlets
g. Liquid inlets and outlet
h. Holddown
i. Nuts and bolts
j. Number of trays
k. Vapor diffusion method
l. Corrosion allowance

The engineering calculations relating to the degasifier at Blueside Company are shown in the Appendix. The current sulfide reclamation was scaled up to a full production unit by Camp, Dresser, McKee, Inc., of Boston, Massachusetts.

Degasifying or stripping is the release of a gas from a solution by contacting the liquid with an inert gas. In sulfide reclamation, acidification to 5.0 - 5.5 pH lowers the solubility of the hydrogen sulfide in the wastewater causing its release from solution. Air serves as the inert gas to strip the gas and move it to the absorber.

Gas absorption is the opposite of stripping; i.e., in absorption, the gas is caused to dissolve into a liquid or react with the liquid.

The limiting amount of a gas dissolving in a liquid at a given temperature and pressure is termed its solubility. The method of determining the limit is to expose the liquid to the gas for a sufficient length of time so that no more gas dissolves at the given temperature or pressure. In order to make the time as short as possible, vigorous mixing of the solution is necessary as well as a relatively large area of contact between the gas and the liquid.

In the solution of/or the reaction of a gas with a liquid, the principle of countercurrent flow is used. The gas is passed first through the almost saturated solution and consecutively through less and less saturated solution and finally through the pure liquid. The gas is commonly introduced at the bottom of the tower, into the top of which the liquid is fed.

The tower may be packed with inert dispersion plastic rings in random fashion or contain bubbling plates to furnish the desired surface of contact and the necessary mixing.

A heat change always accompanies solution of a gas in a liquid.

The process of selective gas absorption is typified by the sulfide reclamation system. The absorption of hydrogen sulfide from a hydrogen sulfide/air mixture occurs in the absorption tower using a sodium hydroxide solution. The air is the inert gas and flows through the tower without reaction.

The absorption tower must be tall enough so that there is sufficient contact time between the gas and the liquid and large enough in cross sectional area so that the required volume of flow can be accommodated. If too much liquid is run down for the size of the tower, then the upward flow of gas will hold up the liquid, causing the tower to flood.

The amount of gas that a liquid can dissolve at a given temperature is determined by Henry's Law, which states that the partial pressure of a gas in equilibrium with a solution is equal to a constant times its concentration in the solution or

$$pa = H\ Xa$$

The constant, H, is different for each system and for each temperature and it must be determined experimentally.

The concentration of the hydrogen sulfide in the flue emission from the absorption tower must be less than the concentration in the sodium hydroxide. The difference between the actual concentration and the equilibrium concentration is necessary in order that there be a driving force to cause absorption to take place.

For each type of absorption tower and set of operating conditions, there is a specific absorption coefficient. This coefficient, K, depends on the type and composition of the gas and solution involved, the type of packing, the temperature, and the gas and liquid flow rates. The coefficient is defined as the amount of material absorbed per unit time, per unit contact area, per unit of driving force. The area of contact through which the gas is being absorbed cannot be measured; therefore, the unknown area is included with the coefficient, K, and determined experimentally as coefficient times the area, Ka. After the amount of material absorbed per unit time is determined for the whole tower by direct measurement, it is divided by the tower volume, and by the driving force giving the final form

$$Ka = \frac{\text{Material Absorbed (lbs)}}{\text{Time (hr)} \times \text{Tower volume (cu ft)} \times \Delta x}$$

where Δx is the driving force. The Δx driving force is the difference between the actual concentration of the liquid and that which it would have if it were in equilibrium with the gas. Since Δx may vary throughout the tower, an average may be used.

For any given installation, the absorption coefficient depends on the liquid flow rate, the gas flow rate, the temperature and concentration of the liquid and gas. Because the open cross-sectional area of the packed tower is not known, the gas and liquid rates are usually given in superficial velocities. This velocity is defined as the velocity the liquid would have if it were flowing through and completely filling the tower when empty of packing. (15, 17)

When the gas being absorbed is very soluble or reacts completely, the liquid rate is not important and the coefficient is affected most by the gas rate.

Absorption need not be performed in a packed tower. It may be done in a bubble cap tower or in a tank where the gas is bubbled through a liquid. If a tank is used, good dispersion of the gas in the liquid is necessary and may be obtained by violent agitation of the liquid with a stirrer or introduction of the gas into the liquid through a porous plate.

One of the first steps in the design of a degasifier or an absorber is to determine how many theoretical trays are required to achieve full liberation of the H_2S to the air flow for the degasifier or full absorption of the H_2S into the sodium hydroxide for the absorber. On a theoretical tray, the concentration of the H_2S is in equilibrium with the H_2S dissolved in the liquid; Henry's Law, $pa = HXa$

Where: pa = partial pressure in the atmosphere of the hydrogen sulfide

Xa = mole fraction of hydrogen sulfide in the liquid

H = Henry's Law constant

Perry's Chemical Engineering Handbook lists data for H_2S in H_2O solution equilibrium at different temperatures. (10, 11) Henry's Law constant for H_2S in H_2O at 20°C is given as

$$H = 4.82 \times 10^4$$

Although the degasifier has a chemical phenomena associated therewith; i.e.,

$$\text{Effluent Sulfides} + H_2SO_4 \rightarrow \text{Effluent Sulfates} + H_2S$$

the reaction kinetics can be assumed instantaneous when compared to the time to achieve vapor-liquid equilibrium.

The fifth data point in Table No. 21 shows that 2.21 pounds/minute of H_2S were fed to the degasifier and 0.02

pounds/minute flowed to the sewer in the degasified effluent leaving 2.19 pounds/minute of H_2S liberated from the wastewater for movement to the absorber. At a molecular weight of 34, the 2.19 pounds represents 6.44×10^{-2} moles/minute of H_2S.

At an air flow rate of 320 cfm having a specific volume of 13.5 cu ft/lb, the air rate is 23.7 pounds/minute. Considering an average molecular weight for air of 29, the air provides 0.817 moles/minute.

The mole fraction of H_2S and air is 7.33×10^{-2} and 0.927 moles/minute respectively. Therefore, the total moles/minute for the overhead gas is 0.872 moles/minute. Allowing 2 psig for pressure drops through the demister pad, piping and absorber, the internal pressure at the top of the degasifier is 1.15 atmosphere (absolute). Thus, the partial pressure for the H_2S is $7.33 \times 10^{-2} \times 1.15$ atmospheres or

$$pa = 8.43 \times 10^{-2} \text{ atmospheres}$$

Calculating for Henry's Law:

$$pa = H\ Xa$$

$$Xa = pa/H$$

$$Xa = 8.43 \times 10^{-2}/4.82 \times 10^{4}$$

$Xa = 1.74 \times 10^{-6}$ mole fractions of H_2S in the liquid

Determining the weight of H_2S remaining in the solution on the theoretical tray requires the calculation of the total moles on the tray. At 240 gpm of influent flow at 8.5 lbs/gallon, the theoretical tray holds about 2,040 pounds/min of solution. Using the molecular weight of the principal component, i.e., water at 18 lbs/mole as a basis for calculation, there are 113.3 moles on the tray. For 113.3 moles/min of water on the tray, there would be:

113.3 moles/min $\times 1.74 \times 10^{-6}$ mole fractions of H_2S

or

1.98×10^{-4} moles of H_2S in the liquid

At a molecular weight of 34 for H_2S, 1.98×10^{-4} moles represents 6.72×10^{-3} or 0.00672 pounds/min of sulfide remaining in the tray's solution.

Since the actual data shows 0.02 pounds/minute of H_2S in the degasifier effluent, no further tray calculations are necessary. The data shows that one theoretical equilibrium tray is required in the degasifier.

To design for one theoretical tray with vigorous agitation and expect equilibrium to be achieved momentarily is inconceivable. The design philosophy provided one tray for acidification, mixing, and distribution, another tray at the bottom for air flow distribution, and two center trays of the same design at an assumed efficiency of 50% to do "the work".

The absorber used in the present sulfide reclamation system is a commercially available unit. However, the same calculations using Henry's Law may be applied to determine its adequacy. Data relating to the liquid-vapor system of the absorber would be used. The calculations for the present absorber indicates its adequacy at design specifications. If flue emission is to be eliminated for higher sulfide input, additional absorption capability is needed.

SECTION 8

OPERATIONAL CHARACTERISTICS OF THE SULFIDE RECLAMATION SYSTEM

The sulfide reclamation system has the following process variables that must be recognized for proper operation:

a. Sulfide content of the degasifier influent and effluent, mg/l
b. Total wastewater volume to be processed daily
c. Influent flow rate, gpm
d. Air flow rate, cfm
e. Acid flow rate, ml/l for acidification to 5.0 - 5.5 pH
f. Liquid levels existing within the degasifier trays
g. Overflow tower outlet setting for controlling liquid levels
h. Absorber type and capacity
i. Caustic soda concentration
j. Caustic soda recirculation rates through the absorber
k. Basic knowledge of sulfide chemistry (covered in the appendix section of this report)

Safety of operation in maintaining a mixture of hydrogen sulfide gas in air below the lower explosive limit of 4% is a governing factor in the operation of the sulfide reclamation system.

The sulfide content in the clarified wastewater must be known and checked periodically prior to and during operation of the system. The sulfide content determines the influent flow rate to be used in relation to the air flow rate. The influent flow rate governs the amount of hydrogen sulfide gas that will be liberated by acidification to a 5.0 - 5.5 pH.

The air flow rate should provide the amount of dilution air to keep the concentration of hydrogen sulfide gas below the lower explosion limit as it flows to the absorber. The relationship of the influent flow rate and air flow rate is that the influent flows governs the sulfide input into the degasifier while the air flow serves to dilute the hydrogen sulfide gas to a safe concentration for reclamation.

The total wastewater volume to be processed daily establishes the sizing of the sulfide reclamation equipment and the degasifier flow rate. Acidification to a 5.0 - 5.5 pH is a

Table No. 6

INFLUENT SULFIDE CONTENTS
VS.
AIR FLOW RATES OUTSIDE OF EXPLOSIVE RANGE

Influent Sulfide, mg/1			200			400			800			1200			1600		
Influent Flow, gpm			100	150	230	100	150	230	100	150	230	100	150	230	100	150	230
Sulfide, lbs./min.			0.17	0.25	0.38	0.33	0.50	0.77	0.67	1.0	1.54	1.0	1.5	2.3	1.34	2.00	3.07
H_2S, lbs./min. to Absorber			0.18	0.27	0.40	0.35	0.53	0.82	0.71	1.06	1.64	1.06	1.59	2.44	1.42	2.12	3.26
Air Flow Rates			% H_2S in Air			% H_2S in Air			% H_2S in Air			% H_2S in Air			% H_2S in Air		
cfm	lbs./min.																
100	7.41	Acceptable Air Flow Rates Are Enclosed	2.4	3.5	5.1	4.5	6.7	9.9	8.7	12.5	18.1	12.5	17.7	24.8	16.1	22.2	30.6
200	14.82		1.2	1.8	2.6	2.3	3.4	5.2	4.6	6.7	9.9	6.7	9.7	12.9	8.7	12.5	18.0
300	22.23		0.8	1.2	1.8	1.6	2.3	3.6	3.1	4.6	6.9	4.6	6.7	9.9	6.0	8.7	12.8
400	29.64		0.6	0.9	1.3	1.2	1.8	2.7	2.3	3.4	5.2	3.4	5.1	7.6	4.6	6.7	9.9
500	37.05		0.48	0.72	1.1	0.9	1.4	2.2	1.9	2.8	4.2	2.8	4.1	6.2	3.7	5.4	8.1
600	44.46		0.40	0.6	0.89	0.78	1.2	1.8	1.6	2.3	3.6	2.3	3.5	5.2	3.1	4.6	6.8
700	51.87		0.34	0.52	0.76	0.67	1.0	1.6	1.4	2.0	3.1	2.0	3.0	4.5	2.7	3.9	5.9
800	59.28		0.30	0.45	0.67	0.58	0.89	1.4	1.2	1.8	2.7	1.8	2.6	3.9	2.4	3.5	5.2

function of the acid pump setting and running time. 0.8 ml/l of acid per liter of influent for each 1.0 pH unit decrease is required. The wastewater at Blueside Company has an average pH of 8.5 and requires 2.7 ml/l of 66° Baume sulfuric acid to lower to 5.0 - 5.5 pH.

The sulfide content in the influent, the influent flow rate, the air flow dilution rates and the concentration of hydrogen sulfide in air enroute to the absorber is shown in Table No. 6. This table defines sulfide reclamation ranges of low to high sulfide bearing wastewater within varying influent flow and/or the air flow for controlling the percent hydrogen sulfide in air to a point below the lower explosive limit.

The design specifications for the sulfide reclamation system set 700 cfm of air flow with a maximum sulfide capture of 700 mg/l from degasifier influent flow of 230 gpm or less. The pounds of sulfide per minute for a degasifier influent of 230 gpm calculates to 1.34 pounds, or 1.42 pounds of hydrogen sulfide gas when the effluent is acidified to 5.0 - 5.5 pH. An air flow of 700 cfm at 13.5 cubic feet per pound of air calculates to 51.85 pounds per minute of air. The percent of H_2S in air flowing to the absorber each minute equals:

$$\frac{1.42 \text{ lbs}/H_2S \times 100}{(51.85 \text{ lbs of air} + 1.42 \text{ lbs } H_2S)} = 2.67\% \ H_2S$$

The percent concentration of hydrogen sulfide in the air flow is well below the lower explosive limit. Table No. 6 shows that a high sulfide bearing influent having 1,600 mg/l can be processed through the sulfide reclamation system at 100 gpm of influent flow and an air flow of 700 to 800 cfm of diluting air allowing for proper reclamation below the lower explosive limit.

Lower sulfide content in the influent will allow the air flow rate to be reduced. A lower air flow would increase the contact time in the absorber. The effective absorbing zone in the present absorber is 11.2 cubic feet. The calculated contact time for the various air flow rates is shown in Table No. 7.

TABLE No. 7

ABSORBER CONTACT TIME AS RELATED TO AIR FLOW RATES

Air Flow, cfm	Contact Time, Seconds
100	6.72
200	3.36
300	2.24
400	1.68
500	1.34
600	1.12
700	0.96
800	0.84
900	0.75
1,000	0.67

The absorber in the present system was built by the Heil Process Equipment Corporation and is listed as their Model 731.5. The high sulfide reclamation of this unit is made possible by its design. The air hydrogen sulfide stream enters the absorber near the bottom and is contacted by a caustic soda solution draining from the packing within the absorber. The air then enters the packing and rises countercurrent to the flow of the caustic soda solution. The route through the packing increases the contact between the air stream and the caustic soda for maximum absorption of the hydrogen sulfide. The air stream is given a final caustic soda wash as it passes through the sprays used for distributing the caustic soda solution over the packing.

The clean air passes through a mist eliminator before leaving the absorber which removes 99% of the entrained moisture. The absorber has the capability to remove 99% of the hydrogen sulfide providing the air flow is no greater than 700 cfm and the recirculation of the caustic soda solution is 20 gpm at 20 psi with a minimum of 10.0 pH. The absorber has a maximum air flow rate of 900 cfm.

The air blower installed in the sulfide reclamation system can deliver 1,000 cfm of air. However, full use will create an imbalance in the total system. A variable drive type of air blower having a maximum air output of 800 cfm would be preferred when degasifier influent and the air flow dilution are considered. Proper and continuous operation of the system requires the air flow to be reasonably unrestricted in its flow through the degasifier to the absorber. The air flows from the air blower through a six inch diameter pipe to the air plenum at the bottom of the degasifier. The air flows through 80 air diffusers in each of the four trays in the degasifier. Each diffuser has 12 orifice openings for air passage. The total area of the orifice openings in the 80 diffusers on a tray is equal

TABLE NO. 8

THEORETICAL OPERATING CONDITIONS FOR 99% SULFIDE RECOVERY

DEGASIFIER TOWER												
Air Flow CFM	Air Pressure psig	Pressure Drop per Level	1st Level		2nd Level		3rd Level		4th Level		Overflow Tower Sight Glass inches	Absorption Tower Caustic pH Circulation
			Press. Gauge psig	Sight Glass inches	Press. Gauge psig	Sight Glass inches	Press. Gauge psig	Sight Glass inches	Press. Gauge psig	Sight Glass inches		
700	8	1.8	6.2		4.4		2.6		1.8-0			Min. pH 10 20 gpm @ 20 psi

Effluent Flow: 200 gpm or below; maximum is 230 gpm Sulfide Absorption Capacity 700 ppm

Height downcomer level physical 39"; No. of bubblers is 80 with 12 orifice openings

ACTUAL OPERATING CONDITIONS

Time (mins)	Air Flow CFM	Air Temp. °F	Console psi	1st Level		2nd Level		3rd Level		4th Level		Overflow Tower Sight Glass inches
				Press. Gauge psig	Sight Glass inches	Press. Gauge psig	Sight Glass inches	Press Gauge psig	Sight Glass inches	Press. Gauge psig	Sight Glass inches	
0		32	7.5	5.0	44	3.5	44.5	2.2	44	0	36	198
30		125	8	5.5	39	4.0	43	2.5	49	0	47	198
60		130	8	5.5	39	4.0	43.5	2.5	49	0	47	198
90		130	8	5.5	39	4.0	43.5	2.5	49	0	46	198
120												
150												
180												
210		130	8	5.5	39	4.0	43.5	2.5	49	0	46	198
240												
270	1080	130	8	5.5	39	4.0	43.5	2.5	49	0	46	198

to the cross-sectional area of the six inch diameter air input. The orifice openings in the diffusers will begin to get clogged with solids from the influent and a back-pressure created. As more orifice openings plug up, the pressure builds to 12 psig signalling the need for an internal cleaning of the degasifier. The section of diffusers with longer service life has not been achieved.

The operating step for starting the sulfide reclamation system begins with the pumping of the clarified effluent to fill the degasifier. The degasifier at start up will have 46 inches of effluent showing in the bottom tray's sight glass. During continuous operation, the clarifier level change per unit time is used to determine flow rate.

The air is provided at a constant rate and is limited by the size of the air blower, the speed and the pressure under which it operates. When the influent flow and air rates are constant, the degasifier will stabilize with levels at each tray in accordance with the pressure in each tray. Table No. 8 compares the theoretical conditions of operations as well as the actual conditions existing during system operation. The theoretical pressure drop from the bottom tray to the top was calculated to be 1.8 psig per tray. In actual operation, the pressure drop for the bottom tray was 2.5, for the second tray, it was 1.5, for the third tray, it was 1.5, and the pressure drop in the top tray was 2.5 psig or an average of 2 psig per tray. The design pressure drop per tray is essentially accurate. At the time these measurements were made, the air flow rate was 1,080 cfm, and three air diffusers were still located below the downcomer in each tray.

The liquid levels as shown by the sight glass readings for each tray indicate a variation in the downward flow of the influent. Flooding is occurring with the top tray holding 46 inches of liquid (after 60 minutes of operation) the third level 49 inches, the second level 43.5 inches and the bottom level at 39 inches. The height of the downcomer in each tray is 39 inches.

The lower tray reflected a condition where some air flow was passing into the downcomer and flowing in part through the overflow tower. The majority of the air flow is countercurrent to the downward flow of the effluent.

The total of the sight glass readings is 178.5 inches. The pressure reading of the air blower was 7.5 psig and corresponds to 207 inches of water pressure for the overflow tower setting. The actual overflow tower setting was 198 inches. The difference between the theoretical and the actual is within the calibration of the pressure gauges. However, since flooding was

TABLE NO. 9

ACID PUMP SETTING VERSUS INFLUENT FLOW IN GALLONS/MINUTE TO REACH pH RANGE 5.0 - 5.5

No. of Open Turns on Influent Pump Valve	Flow in Gallons/ Minute	Liters of Influent/ Minute	mls. of Acid/Liter Required	Total mls. of Acid Required	Acid Pump Setting
	50	189.25	2.7	511	72
0.7 - 0.75	60	227.1	2.7	613.7	82
	75	283.88	2.7	766	109
1.0	80	302.8	2.7	818	116
	100	378.5	2.7	1022	146
	125	473.13	2.7	1277	175
	150	567.75	2.7	1533	205
	175	662.38	2.7	1788	238
2.5	200	757.0	2.7	2044	280
	250	946.25	2.7	2555	351

occurring, the overflow tower setting should have been increased to compensate.

The levels of solution in the degasifier are controlled by the overflow tower outlet pipe setting. In the overflow tower, the outlet pipe is sleeved into a stand pipe allowing it to be raised or lowered. This adjustment capability permits the degasifier to be operated at varying pressures.

For the studies in this report, the level was established at a steady flow and remained constant. When the diffusers in the degasifier are clean, the height of the overflow tower outlet is set for an operating pressure of 7 psig which converts to 193.7 inches of height or, 27.67 inches of water per psig. When clogging occurs this height is reset to a maximum of 12 psig.

The liquid effluent from the degasifier flows directly to the city sewer system. Initially provision was made for chlorination of unremoved sulfide. Hydrogen peroxide is also suitable for the trace sulfide removal. Present costs indicate that oxidation using hydrogen peroxide is more economical on a standby basis. Under normal operation at a 5.0 - 5.5 pH, data shows that the sulfide remaining is essentially zero. The need for oxidation is, therefore, limited and the cost for oxidation is negligible under proper operation. Under upset operation, the quantity of oxidizing agent needed increases very significantly. This will be discussed later in a separate analysis of total costs.

The sulfide bearing influent entering the degasifier is acidified with sulfuric acid. The sulfuric acid is fed at a constant rate by pump under manual operation. The operator measures the pH of the effluent and adjusts the pumping rate of the acid. From the pH of the influent, the operator can make desired setting on the acid pump as shown in Table No. 9. The acid enters the top of the degasifier and mixes with the incoming sulfide bearing wastes within the liquid zone. Complete mixing is obtained by the turbulence in the solution caused by the bubbles of air. The sulfide is converted to hydrogen sulfide in accordance with the equation:

$$\text{Effluent Sulfides} + H_2SO_4 \rightarrow \text{Effluent Sulfates} + H_2S\uparrow$$

The ionization of hydrogen sulfide at pH 5.5 is less than 5% assuring 95% of the hydrogen sulfide as the molecule rather than the ion. The hydrogen sulfide then mixes with the air stream and is carried to the absorber. The degasifier has four trays. Acidification takes place on the top tray. Two central trays provide further diffusion of the H_2S. The bottom tray is used as a dis-engaging zone for the liquid and air stream.

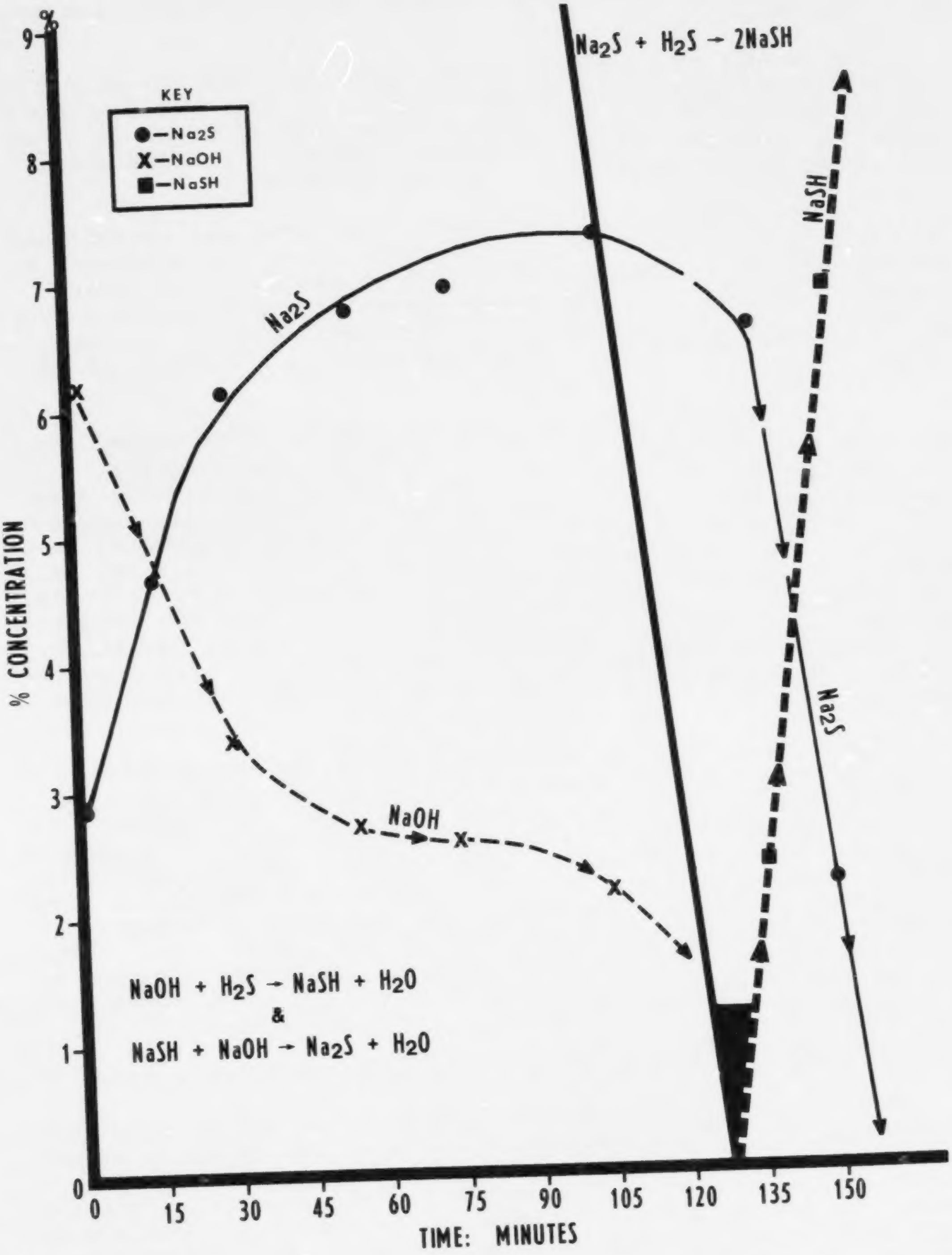


Figure 8. Absorber sulfide capture progression.

The degasifier influent flows downward through the degasifier, countercurrent to the air. The four tray degasifier tower assures a good removal of the hydrogen sulfide. A demister above the top tray prevents the carry over of acid wastes to the absorber.

The absorber, as previously described, has caustic soda solution recirculating from a batch tank through the absorber. The hydrogen sulfide is absorbed by the caustic soda in accordance with the following equations which occur simultaneously in the presence of excess caustic soda:

$$HSH + NaOH \rightarrow NaSH + H_2O$$

and

$$NaSH + \overset{\text{Excess}}{NaOH} \rightarrow Na_2S + 2\ H_2O$$

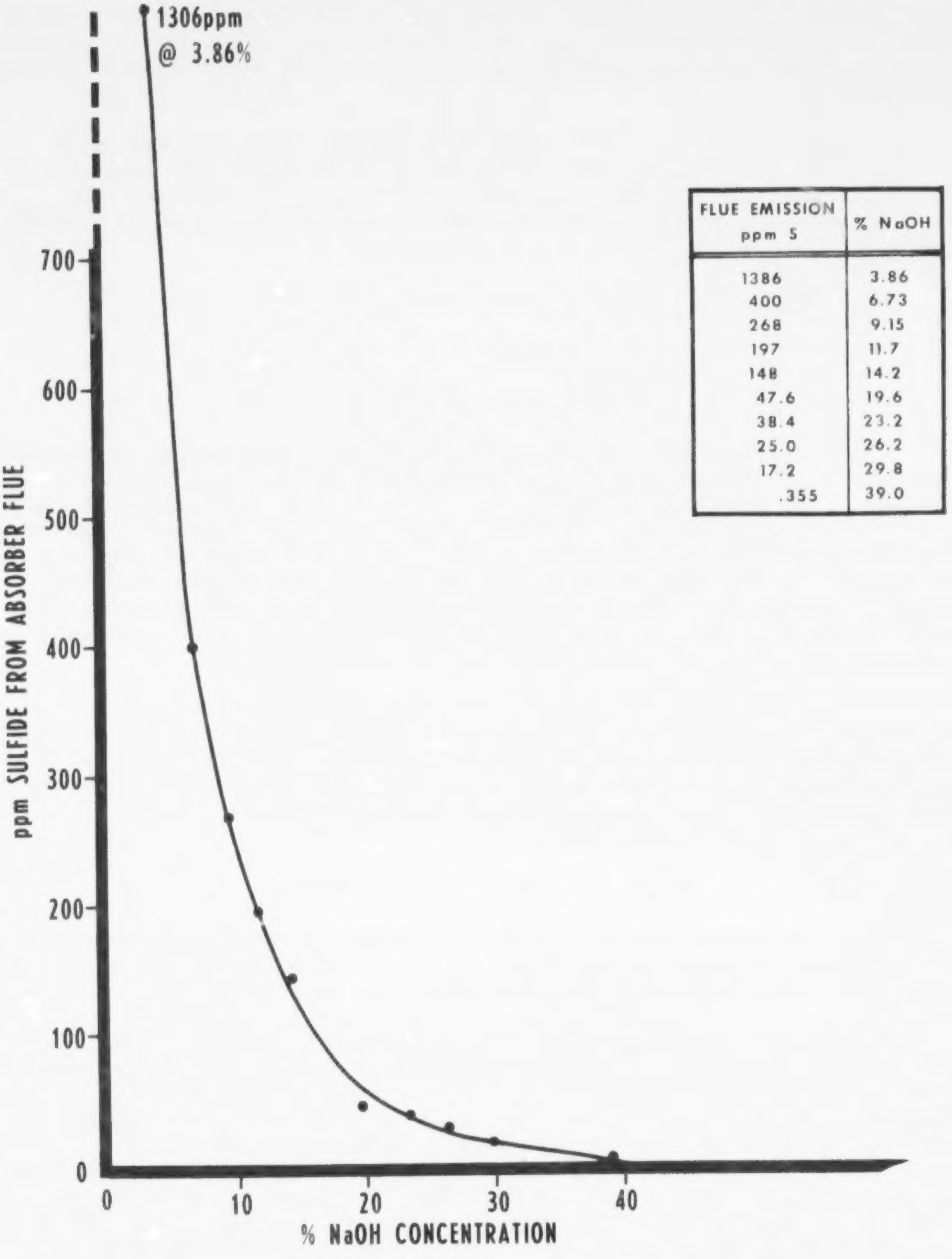
When the caustic soda solution is depleted having absorbed hydrogen sulfide to where the efficiency of the absorption process is decreased, a discharge of hydrogen sulfide will occur from the absorber flue. Control analyses were conducted during system operation on the caustic recirculation tank at regular intervals. When the analysis indicates 2% residual caustic soda, a change is made to the other batch tank containing fresh caustic soda. The saturated tank is analyzed for sodium sulfide content and is sent to storage for tannery recycle.

If the tank at 2% caustic soda residual was allowed to recirculate through the absorber for a prolonged period of time in the presence of excess hydrogen sulfide (as indicated by $H2S$ emitting through the absorber flue) the reaction would proceed as follows in the absence of caustic soda, resulting in the formation of sodium sulfhydrate:

$$Na_2S + HSH \rightarrow 2\ NaSH$$

Table No. 10 shows the progressive change in chemical composition of the caustic soda in the tank as it is circulated through the absorber. The data is also presented in Figure No. 8.

Figure No. 8 illustrates the formation of sodium sulfide proceeding gradually until approximately 2% caustic soda remains. From this point on, hydrogen sulfide readily consumes the residual caustic soda and proceeds to react with the sodium sulfide to form sodium sulfhydrate. This reaction of sulfhydrate formation requires an excess of hydrogen sulfide to exist. This is not a desirable mode of operation as hydrogen sulfide is discharged from the absorber flue. The flue emission becomes excessive after approximately two hours of sulfide reclamation for each fresh tank of caustic. Tanks of circulating caustic are routinely switched each two hours of operation



FLUE EMISSION ppm S	% NaOH
1386	3.86
400	6.73
268	9.15
197	11.7
148	14.2
47.6	19.6
38.4	23.2
25.0	26.2
17.2	29.8
.355	39.0

Figure 9. Sulfide flue emission vs. caustic soda concentration.

TABLE NO. 10

ANALYSIS OF CAUSTIC SODA SOLUTION TANK
AS SULFIDE ABSORPTION PROCEEDS

	COMPONENT ANALYSIS, Percent		
Elapsed Time	Na_2S	NaHS	NaOH
0 mins.	2.85	-	6.2
15 mins.	4.68	-	4.68
30 mins.	6.13	-	3.36
55 mins.	6.75	-	2.72
75 mins.	6.91	-	2.56
105 mins.	7.3	-	2.12
135 mins.	6.56	2.35	-
150 mins.	2.2	6.84	-

The flue emission analyses for sulfides from several trial runs was also correlated with the analyses of the caustic soda concentration. The data relationship which is shown in Figure No. 9.

The effectiveness of the absorber is directly related to the concentration of the caustic soda circulating through the absorber. At higher caustic soda concentrations, the flue emission decreases. As the caustic soda concentration decreases, the flue emission of hydrogen sulfide gas increases.

There are several factors that contribute to the effectiveness of the absorber. At high alkaline pH, the hydrogen sulfide present above solutions can be calculated using Henry's Law. An example of the calculation is made part of the Appendix of this report. Specifically, if the caustic solution had a 12.24 pH, and contained 10% sodium sulfide, there should only be 100 ppm of hydrogen sulfide existing above the surface of the solution. In actual trial runs, this was not the case. A pH of 13.2 allowed for 400 ppm of sulfide emission to the atmosphere which would reflect the air flow influence on the absorption capacity. The efficiency of the caustic spray to coat all of the packing in the absorber is necessary to ensure intimate contact with the available caustic soda solution. In the present absorber, there is no spray head to coat the packing. The caustic soda is caused to flow onto the packing through an 18 inch long pipe that has 0.25 inch holes every 2 inches. The caustic soda flows through the holes to the packing. A possibility that the full packing is not uniformily coated with caustic soda exists. The recirculation rate of the caustic soda through the absorber in relation to the hydrogen sulfide flow is important. Design specifications called for a recirculation rate of 20 gpm. During the course of the project, the motor on the recirculation pump short-circuited and was

TABLE NO. 11

CAUSTIC SODA RECIRCULATION RATES IN RELATION TO SULFIDE AND CAUSTIC SODA IN ABSORBER AT VARIOUS DEGASIFIER INFLUENT FLOWS

Influent Sulfide Data:	800 mg/l at 230 gpm or 1.54 pounds of Sulfide per Minute							
Recirculation Rate, gpm	5		10		15		20	
NaOH, % Concentration	10	2	10	2	10	2	10	2
NaOH, lbs./gallon	0.926	0.17	0.926	0.17	0.926	0.17	0.926	0.17
NaOH, lbs./minute Available in Absorber	4.63	.85	9.26	1.7	13.80	2.55	18.52	3.4
H_2S from Degasifier, lbs./Mintue into Absorber	1.64	1.64	1.64	1.64	1.64	1.64	1.64	1.64
NaOH, lbs./minute Required to React with Sulfide	1.93	1.93	1.93	1.93	1.93	1.93	1.93	1.93
Influent Sulfide Data:	800 mg/l at 150 gpm or 1.0 pounds of Sulfide per Minute							
H_2S from Degasifier, lbs./Minute into Absorber	1.06	1.06	1.06	1.06	1.06	1.06	1.06	1.06
NaOH, lbs./minute Required to React with Sulfide	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
Influent Sulfide Data:	800 mg/l at 100 gpm or 0.67 pounds of Sulfide per Minute							
H_2S from Degasifier, lbs./Minute into Absorber	0.71	0.71	0.71	0.71	0.71	0.71	0.71	0.71
NaOH, lbs./Minute required to React with Sulfide	0.84	0.84	0.84	0.84	0.84	0.84	0.84	0.84

changed. The available motor installed on the pump had a different speed. The recirculation rate dropped to 16 gpm. Table No. 11 relates the recirculation rates to the sulfide and caustic soda present in the absorber each minute at various influent flow rates.

A degasifier influent sulfide content of 800 mg/l was considered at influent flows of 230, 150, and 100 gpm. Table No. 11 lists the pounds of caustic soda that would be present if a 10% or 2% concentration was recirculated through the absorber. The recirculation rates considered are 5, 10, 15, and 20 gpm. The pounds of hydrogen sulfide present in the absorber for the various influent flows are shown.

To simplify recirculation rate analysis, Table No. 12 shows the ratio of caustic soda to H_2S at the two caustic soda concentrations and degasifier influent flows. As the recirculation rate increases, the available caustic soda increases regardless of influent flows. As the influent flow decreases, the sulfide input decreases and the ratio of caustic soda increases regardless of recirculation rates.

A higher ratio of caustic soda to hydrogen sulfide beyond the stoichiometric requirement ensures better absorption. A prior series of experiments relating caustic concentrations to H_2S emission from the absorber flue showed that emission was minimized by high caustic availability in the absorber.

The 2% caustic soda residual in sodium sulfide is considered the end point for changeover to a fresh 10% concentration. At the 5 gpm recirculation rate, insufficient caustic soda is available at 230 and 150 gpm of influent flow. When the caustic soda reaches 0.7%, H_2S would be emitting freely at 100 gpm. At 15 gpm, H_2S would be emitting freely at 1.65, 1.05, and 0.75% caustic soda concentrations at influent flows of 230, 150, and 100 gpm respectively. At 20 gpm, H_2S would be emitting freely at 1.65, 1.08, and 0.8% caustic soda concentrations at influent flows of 230, 150, and 100 gpm respectively.

TABLE NO. 12

RATIO OF CAUSTIC SODA TO HYDROGEN SULFIDE AT VARIOUS INFLUENT AND CAUSTIC RECIRCULATION RATES

Caustic Recirculation Rate into Absorber, gpm	5		10		15		20	
NaOH, % Concentration	10	2	10	2	10	2	10	2
Influent Flow Rate, gpm								
230	2.82	0.52	5.65	1.03	8.47	1.55	11.3	2.1
150	4.36	0.80	8.73	1.6	13.1	2.4	17.5	3.2
100	6.52	1.2	13.0	2.4	19.6	3.59	26.1	4.8

SECTION 9

DATA ANALYSIS

INITIAL OBSERVATIONS

Initial evaluations during 1971 - 72 of the sulfide reclamation system were conducted for several hours each day subject to system problems existing at the time. Minimal data was obtained during these early trials. Only one air flow rate of 1,000 cfm was used. The data consisted of recording the sulfide content of the degasifier influent and effluent once per trial run. This data did not provide an adequate analysis of the system.

Data relating to these early trials is typified by Table No. 13 which relates to the end of 1971 and the beginning of 1972. The tannery's production during this time period was 5,000 to 6,000 hides per week.

The test method for sulfides used initially indicated residual sulfide present in the degasifier effluent at levels of 4 - 5.5 pH. This is not theoretically correct. In later evaluations, the test method was changed because of interference attributed to the iodine demand of the coagulated protein.

Test runs conducted in 1975 - 1976 were specifically designed to obtain data that would provide system evaluation. Samples were collected at 30 minute time intervals for the degasifier influent and effluents and at the caustic soda recirculation tanks to the absorber. Air flow and influent flow measurements were made and the sulfide emission levels at the absorber flue were evaluated.

TEST RUNS AFTER MODIFICATIONS OF THE WASTEWATER TREATMENT SYSTEM

Table No. 14 lists data collected from typical daily runs in 1976.

The tannery's production during this time period averaged 21,700 hides per week or 3,617 per day.

The data in Table 14 shows that the effective removal of sulfide is dependent upon the pH of the effluent from the degasifier. Effective sulfide removal was attained at pH's of 5.9 and below. At pH above 6, the effectiveness of sulfide

TABLE NO. 13

SUMMARY OF OPERATING RESULTS SULFIDE RECLAMATION PLANT (1971 - 1972)

		DEGASIFYING TOWER INFLUENT						DEGASIFYING TOWER EFFLUENT					
HOURS OPERATED	RATE OF FLOW gpm	pH	ALKALINITY (ACIDITY) mg/l CaCO$_3$	SETTLEABLE SOLIDS ml/l	TOTAL SOLIDS mg/l	SUSPENDED SOLIDS mg/l	SULFIDE mg/l S=	pH	ALKALINITY (ACIDITY) mg/l CaCO$_3$	SETTLEABLE SOLIDS ml/l	TOTAL SOLIDS mg/l	SUSPENDED SOLIDS mg/l	SULFIDE mg/l S=
2.58	170	9.8	4375	5	26720	3280	280	5.15	70	245	28228	2080	33
1.	150	9.5	2914	3.5	27480	1820	211	5.1	425	250	25740	2660	38
1.58	200	9.0	2400	3	27660	1130	-	4.8	700	30	28000	1265	4.0
2,58	180	9.2	2470	2.5	27530	1220	-	5.1	425	10	27333	1340	87
2.42	180	9.2	2791	3	28510	1880	216	5.0	640	250	28046	1780	58
2	180	9.4	2841	4.5	26890	2020	326	5.5	360	240	27590	2200	17.6
2.08	180	9.7	3887	3	26970	1660	504	5.0	540	250	28860	2140	51.0
2.0	180	9.6	3591	2	30340	2366	260	5.4	1474	100	29330	3320	16.0
1.83	180	9.65	3945	4	29990	2267	-	6.2	1890	260	32770	3166	16.8
2.25	180	8.9	3360	4	32410	2925	-	6.0	-	110	31500	1900	32
2	180	9.4	-	9	28450	3040	220	4.65	-	200	26545	3220	28
1.25	180	9.4	-	3	27900	2680	-	4.7	792	150	25640	2140	14.4
-	-	9.6	3321	8	24140	2320	-	6.2	1955	200	30460	2860	11.0
-	-	9.2	3704	3	29900	2000	130	5.1	-	300	32970	2520	24
1.25	180	9.4	3351	3	30080	2300	246	6.4	187	150	26400	2780	52
1.66	150	9.4	2937	3	50000	2860	400	5.6	620	206	25140	1240	42
2.0	180	9.8	4375	5	26720	3280	280	4.65	-	200	17730	2870	28
4	200	8.4	1800	10	27840	1403	210	5.1	425	250	25140	2620	38
-	-	9.1	3137	3	-	1500	208	5.1	-	110	32510	2540	24

TABLE NO. 14

SUMMARY OF OPERATING RESULTS SULFIDE RECLAMATION PLANT - (1975-1976)

		DEGASIFYING TOWER INFLUENT						DEGASIFYING TOWER EFFLUENT					
HOURS OPERATED	RATE OF FLOW gpm	pH	ALKALINITY (ACIDITY) mg/l $CaCO_3$	SETTLEABLE SOLIDS ml/l	TOTAL SOLIDS mg/l	SUSPENDED SOLIDS mg/l	SULFIDE mg/l S=	pH	ALKALINITY (ACIDITY) mg/l $CaCO_3$	SETTLEABLE SOLIDS ml/l	TOTAL SOLIDS mg/l	SUSPENDED SOLIDS mg/l	SULFIDE mg/l S=
4.16	240	8.6	3450	7	30180	3660	1000	5.8	0	325	32500	3800	0
3.67	248	8.5	2880	14	23100	2000	1000	5.8	10	195	26600	3700	0
4.0	228	8.6	3700	24	32900	1500	400	5.5	20*	210	26600	6566	0
2,33	201	8.6	3460	28	26200	1750	1140	5.5	25*	388	39050	6650	0
5.0	255	8.6	3550	19	22350	1200	1440	6.7	750	180	26800	3850	40
4.5	240	8.6	3400	17	30160	2100	500	4.0	110*	317	31850	2600	0
4.5	289	8.7	3600	10	20650	3200	1080	6.8	700	467	25200	3150	360
9.25	216	8.8	3550	8.5	24350	1850	1400	6.8	725	562	24400	2100	320
4.25	193	8.9	3300	17	28200	3300	1400	5.0	20*	275	28950	3200	0
2.08	217	8.6	3550	9	29060	2750	1200	3.6	130*	380	31800	1800	0
3.75	167	8.8	3700	32	27650	3050	1120	6.2	600	462	25100	3500	120
3.0	192	9.1	3450	6.5	20950	1550	760	5.6	25*	588	32050	5100	0
4.75	193	8.5	3600	11.2	25250	2100	600	5.9	10	210	29850	2250	0
1.08	216	8.5	3800	4.5	30200	1750	540	4.1	100*	400	33300	6850	0
2.92	248	8.8	3850	15	30550	3050	1240	5.5	15*	250	26650	2150	0

removal was not assured and at pH 6.8, the sulfide removal was poor. The graph, Figure No. 10 is theoretical relationship of the effect of acidification and the liberation of hydrogen sulfide from sulfide solutions at various pH levels. Correspondingly, the graph relating to sulfide remaining in the degasifier effluent correlates reasonably well.

At pH of 6.0, 89% of the hydrogen sulfide should be liberated from the sulfide effluent. The actual data shows that 91% has been removed. At pH 6.8, 55% should be liberated from the solution, the actual data shows 76% sulfide has been removed from the effluent.

The acidification increased greatly the settleable solids, suspended solids, and the total solids. This is due to the precipitation of the solubilized protein. (Reference Table No. 15, Figures 11, 12, 13). The flow rate of the degasifier effluent, within the tested range, has no effect on the efficiency of sulfide removal. Complete removal of the sulfide from the effluent can be achieved by the system.

Specific trial runs were made for the analysis of the overall efficiency of the component parts of the system; i.e., the degasifier, the absorber, the recirculating caustic soda solution concentrations, the influent flow, the air flow, and the absorber flue emission.

The test to demonstrate the effectiveness of the absorption as the sodium hydroxide solution reached the limit of absorption capacity is summarized in Table No. 16. The influent data shows the variations in the sulfide during the day. The amount of sulfide can be calculated as:

Flow (gpm) x 8.3 x time (minutes) x sulfide (mg/l) = lbs sulfide

The sulfide in the effluent can be calculated by the same formula. The difference between the sulfide in the influent and the sulfide in the effluent is the amount of sulfide in the air going to the absorber.

In the absorber, the reaction between hydrogen sulfide and sodium hydroxide is as follows:

$$H_2S + NaOH \rightarrow NaSH + H_2O$$

Therefore, the decrease in the sodium hydroxide is equal to the sulfide absorbed on a mole to mole ratio. From the analysis of the caustic soda solution the amount of sulfide removed from the air is determined. The difference between the amount of sulfide received by the absorber and that found in the caustic soda solution is the amount lost to the atmosphere from the absorption tower flue.

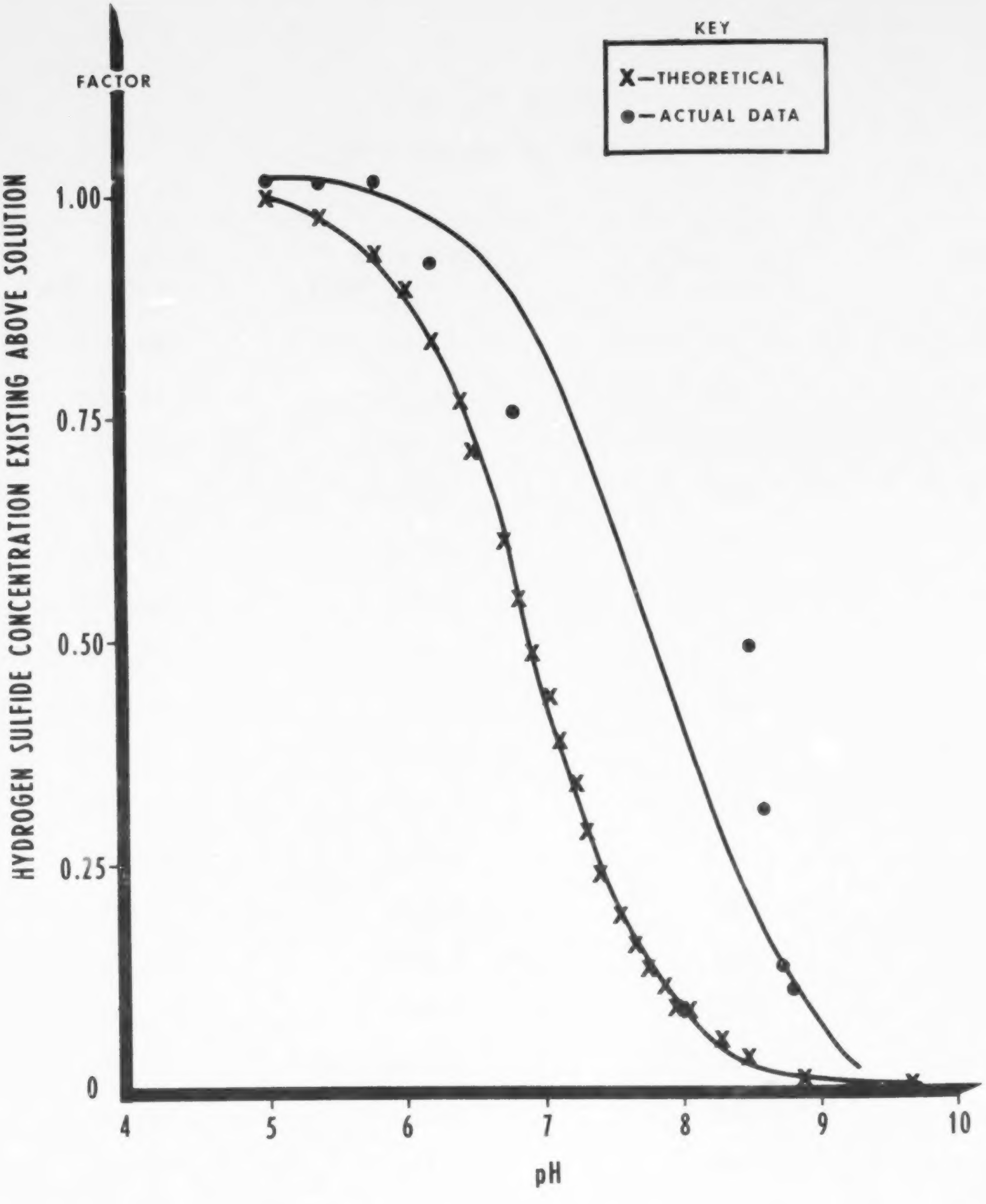


Figure 10. Effect of pH on sulfide removal.

TABLE NO. 15

SUMMARY OF SOLIDS DATA

pH	Total Settleable Solids, mg/l	Suspended Solids, mg/l	Total Solids, mg/l
9.1	--	1,550	20,950
8.9	17.5	3,300	28,200
8.8	18.5	2,650	27,517
8.7	10	3,200	20,650
8.6	17	2,160	28,475
8.5	9.9	1,950	26,183
6.8	515	2,625	25,200
6.7	180	3,850	25,600
6.2	462	3,500	25,100
5.9	210	2,250	29,850
5.8	260	3,750	29,550
5.6	588	5,100	32,050
5.5	283	5,122	30,750
5.0	275	3,200	28,950
4.1	400	6,850	33,300
4.0	317	2,600	31,850
3.6	380	1,800	31,800

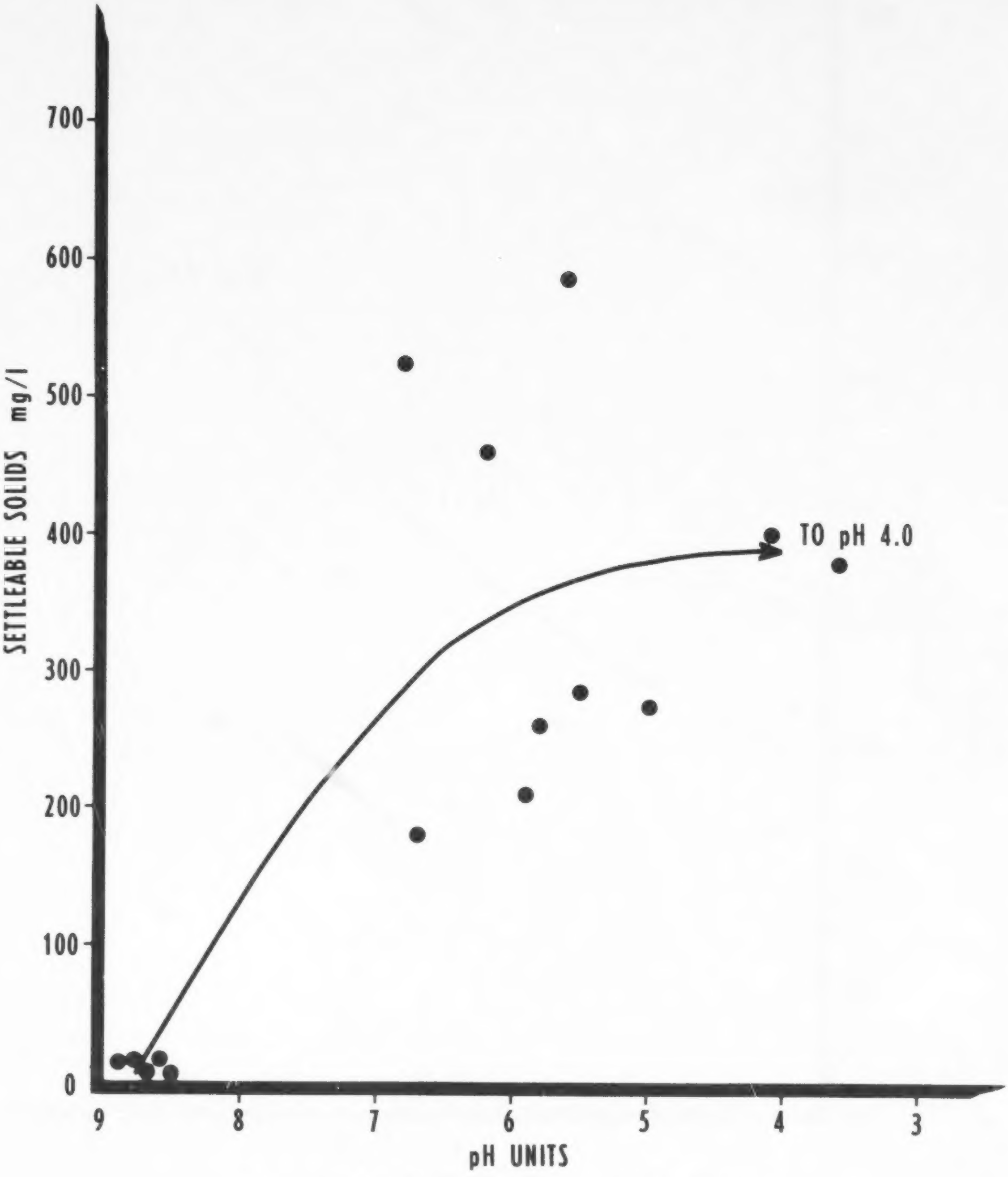


Figure 12. Effect of pH on suspended solids.

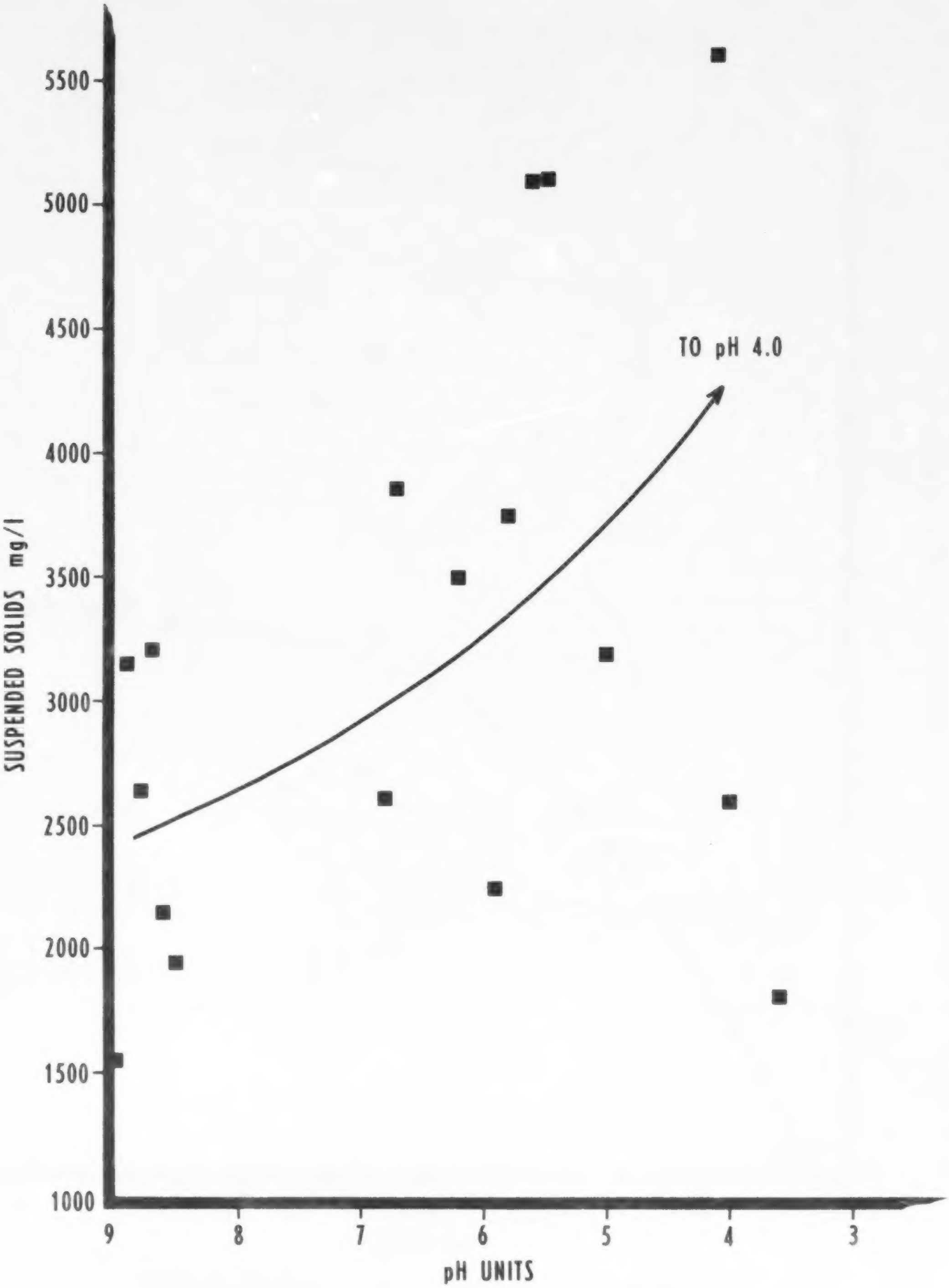


Figure 12. Effect of pH on suspended solids.

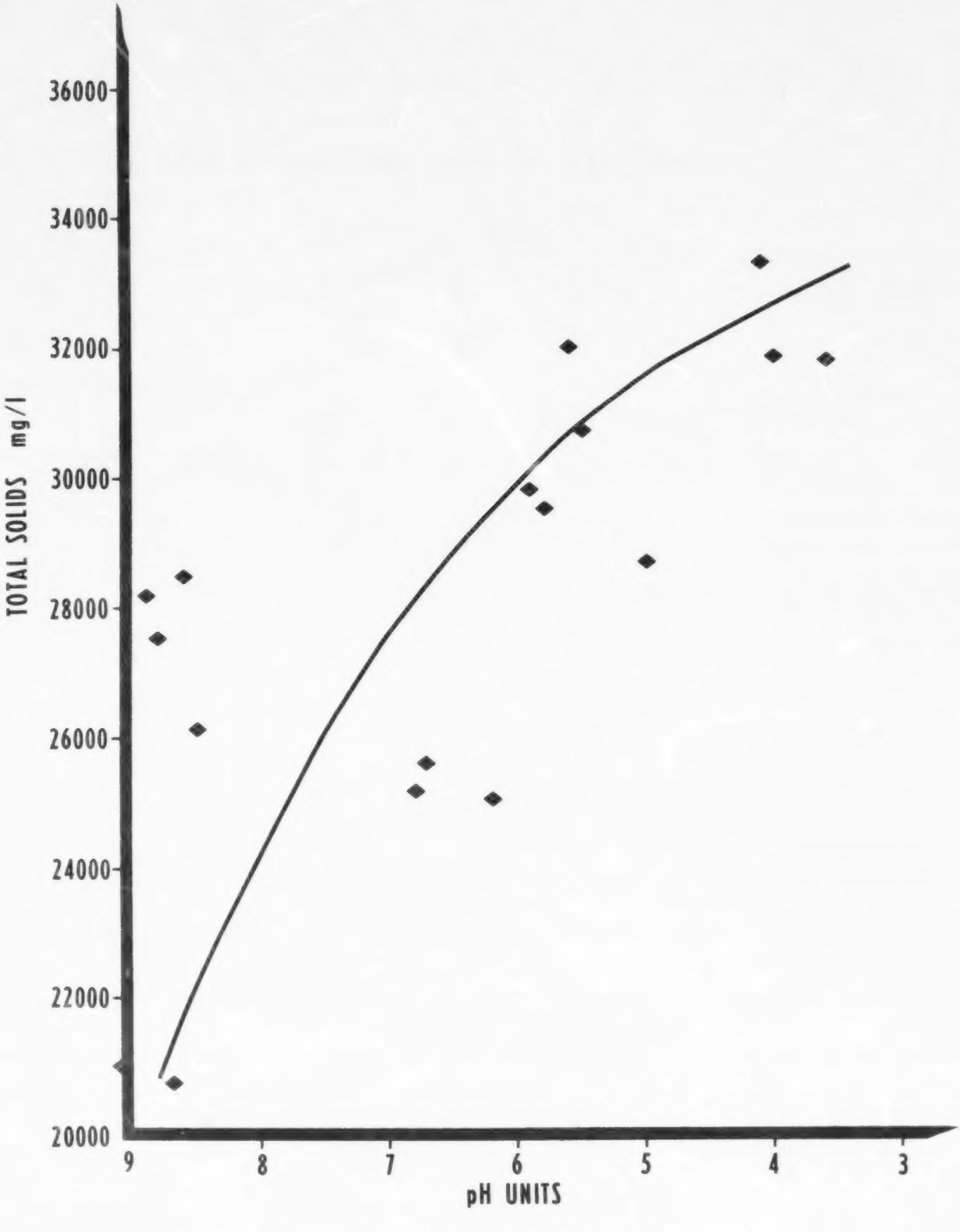


Figure 13. Effect of pH on total solids.

TABLE NO. 16

DEGASIFIER INFLUENT AND EFFLUENT DATA

INFLUENT

Time (mins.)	0	60	120	180	240	300
pH *	8.9	8.9	8.9	8.8	8.9	8.9
Suspended Solids (mg/l)	2,500	2,700	2,600	2,500	3,300	3,200
Total Solids (mg/l)	30,300	30,800	30,700	30,700	31,200	31,300
Settleable Solids (mg/l)	.5	.1	5	4	8	7
Sulfide (mg/l)	1,280	1,240	1,040	960	1,040	920

EFFLUENT

pH*		4.5	4.9	4.5	3.75	3.9
Suspended Solids (mg/l)		3,930	3,700	4,470	3,800	3,900
Total Solids (mg/l)		33,400	33,600	34,400	34,400	34,600
Settleable Solids (mg/l)		390	409	660	300	300
Sulfide (mg/l)		40	0	0	0	0

* Standard Unit

TABLE NO. 17

ABSORBER DATA

Time, min	0	60	120	180	240	300
Specific Gravity	1.120	1.16	1.114	1.112	1.111	1.10
NaOH, Volume, gal	466	474	483	491	499	510
NaOH Solution, lbs	4,355	4,414	4,490	4,556	4,626	4,681
pH*	13.4	13.3	13.2	12.8	12.7	12.1
NaOH, %	13.2	9.5	6.5	4.26	2.4	1.7
NaOH, lbs	574.8	419.6	291.8	194.0	110.0	79.6
NaOH, lbs/hr		155.2	127.8	97.8	84.0	30.4
Sulfide, lbs/hr		124.2	102.2	78.2	67.2	24.3
Sulfide, lbs/hr from Degasifier		-	104.5	111.3	122.4	120.0
Sulfide Absorbed, %		-	97.8	70.3	54.9	20.2
Sulfide lost to atmosphere, %		-	2.2	29.7	45.1	79.8

*Standard units

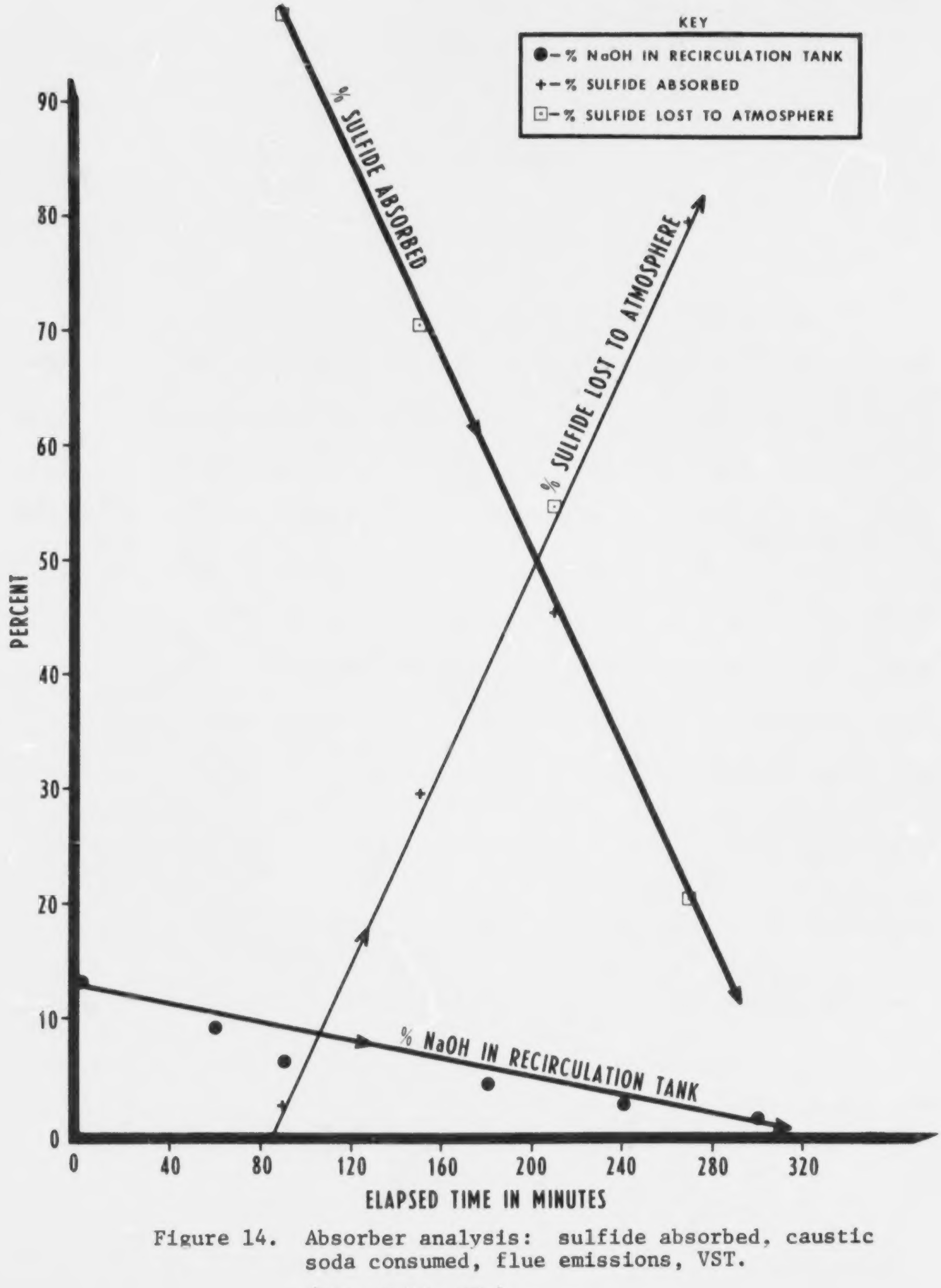


Figure 14. Absorber analysis: sulfide absorbed, caustic soda consumed, flue emissions, VST.

(Ref. Table 17.)

TABLE NO. 18

DEGASIFIER SULFIDE RATES

Time	0		60		120		180		240		300
Sulfide Influent Rate, lb/min	2.37		2.30		1.93		1.78		2.30		1.70
Average		2.335		2.112		1.855		2.04		2.00	
Sulfide Effluent Rate, lb/min	2.37		0.74		0		0		0		0
Average		1.63		0.37		0		0		0	
Sulfide Influent, lbs				126.7		111.3		122.4		120.0	
Sulfide Effluent, lbs				22.2		0		0		0	
Sulfide to Absorber, lbs				104.5		111.3		122.4		120.0	

No method of analysis for the exhaust air was available resulting in the need to determine flue emission on a subtractive basis. The sulfide reclamation equipment as now in use will remove essentially all hydrogen sulfide generated. As the caustic becomes depleted the efficiency of the hydrogen sulfide absorption will rapidly approach zero.

The amount of sulfide absorbed at any time can be determined from the strength of the caustic soda solution. During the second hour, from Table No. 17, the amount of caustic soda used was 127.8 lbs, or 3.195 moles (lb moles). The sulfide absorbed was also 3.195 lb moles or 102.2 lbs of sulfide.

From the influent and effluent data, the amount of hydrogen sulfide flowing from the degasifier is:

Sulfide rate = Average mg/l sulfide x flow (gpm) x 8.345 lbs/gal.

= 1,140 x 222 x 8.345 = 2.112 lbs/min or 126.7 lbs/hr.

Based on this method, the hourly rates for sulfide flow and absorption were calculated. Table No. 18 and Figure No. 14 provide the results.

The data shows the system is working well during the first two hours with very little loss to the atmosphere. As the caustic soda is depleted there is less efficiency in the take-up.

In the existing system, hydrogen sulfide gas will be found in the absorption tower flue emission when the caustic soda is approximately 7% concentration. This emphasizes the need of a correction in the present design of the system. More absorption capacity, or possibly a second absorber would correct this problem.

The data for material balance (Tables 19, 20, 21) was obtained during a test run where analyses of all flows were made at specific time intervals of 30 minutes for a duration of four hours. Chemical analyses were conducted on the influent and effluent for pH, Alkalinity to pH 5.5, Suspended Solids, Total Solids, Settleable Solids, Sulfate, and Sulfide.

The influent flow rate was determined by the time needed to fill the degasifier. The flow rate was found to be 247 gallons per minute.

Sulfide concentration of the influent and effluent as related to the influent flow rate allow the pounds of sulfide removed from the influent to be calculated. A slight error in

TABLE NO. 19

MATERIAL BALANCE DEGASIFIER - INFLUENT*

Sample Identity	1	2	3	4	5	6	7	8	9
Time	12:00	12:30	13:00	13:30	14:00	14:30	15:00	15:30	16:00
Elapsed Time, Minutes	0	30	60	90	120	150	180	210	240
pH	8.9	8.9	8.9	9.0	8.9	8.9	8.8	9.0	8.8
Alkalinity to pH 5.5 mg/l $CaCo_3$	4,278	3,945	4,000	3,806	3,778	3,695	3,834	1,182	1,099
Total Suspended Solids, mg/l	8,620	8,060	8,220	8,840	7,180	6,760	8,000	8,160	6,700
Settleable Solids, mg/l	240	220	220	220	230	220	200	210	230
Total Solids, mg/l	36,050	35,560	34,340	34,720	35,500	34,450	35,840	35,440	35,240
SO_4, mg/l	3,596	-	-	-	5,728	-	-	-	5,586
Sulfide, mg/l	1,228	1,200	1,316	1,062	1,078	741	1,078	1,182	1,099

*Flow Rate 247 gpm

TABLE NO. 20

MATERIAL BALANCE - DEGASIFIER EFFLUENT

Sample Identity	1	2	3	4	5	6	7	8	9
Time	12:00	12:30	13:00	13:30	14:00	14:30	15:00	15:30	16:00
Elapsed Time	0	30	60	90	120	150	180	212	240
pH	6.9	6.7	7.3	6.3	5.4	5.3	5.2	5.3	5.1
Alkalinity to pH 5.5 mg/l $CaCO_3$	417	361	472	111	0	0	0	0	0
Total Suspended Solids,mg/l	6,400	6,160	6,680	6,100	3,700	2,960	5,980	5,940	5,760
Settleable Solids, mg/l	620	550	470	740	550	490	930	870	870
Total Solids, mg/l	37,020	36,190	38,930	32,770	35,340	34,050	36,350	37,980	38,320
SO_4, mg/l	9,333	-	-	-	9,757	-	-	-	10,172
Sulfide, mg/l	87	50	98	14	10	0	0	0	0

TABLE NO. 21

MATERIAL BALANCE - DEGASIFIER INFLUENT AND EFFLUENT SULFIDE RATES

Number	1	2	3	4	5	6	7	8	9
Sulfide Rate, lb/min									
INFLUENT	2.52	2.46	2.69	2.18	2.21	1.52	2.21	2.32	2.20
EFFLUENT	.18	.10	.20	.03	.02	0	0	0	0
Average Sulfide Rate, lb/min									
INFLUENT	2.49	2.56	2.43	2.19	1.86	1.86	2.27	2.26	
EFFLUENT	.14	.15	.12	.02	.01	0	0	0	
Sulfide/lbs.									
INFLUENT	74.7	77.4	72.8	65.7	55.8	55.8	68.0	67.8	TOTAL 538.0
EFFLUENT	4.2	6.0	3.6	.6	.3	0	0	0	14.7
To Absorber	70.7	71.4	69.2	65.1	55.5	55.8	68.0	67.8	523.3

TABLE NO. 22

MATERIAL BALANCE RUN - ABSORBER ANALYSIS*

Sample Identity	1	2	3	4	5	6	7	8	9
Time	12:00	12:30	13:00	13:30	14:00	14:30	15:00	15:30	16:00
Temperature, °F	96	100	102	106	108	112	114	112	112
Volume, gal.	704	710	720	726	731	737	742	748	753
Density, Specific gravity	1.179	1.1695	1.1695	1.166	1.166	1.1555	1.1555	1.1510	1.1510
NaOH Initial Solution, lbs.	6,926	6,929	7,027	7,064	7,113	7,106	7,155	7,185	7,233
pH	13.7	13.5	13.5	13.5	13.45	13.3	13.2	13.3	13.2
NaOH, %	14.2	12.89	11.69	10.33	9.15	8.07	6.73	5.47	3.86
Sulfide, %	2.74	3.80	4.68	5.48	6.55	7.52	7.87	8.84	9.90
Sulfide, % Absorbed	73.6	65.6	58.2	78.8	68.5	28.7	72.0	81.0	
NaOH, lbs	90.4	71.6	77.7	93.0	77.4	91.9	88.5	113.8	

*Flow rate of NaOH recirculation = 16 gpm the calculated values is present and is related to a dwell time of 0.75 hours for the influent passage through the degasifier. Since the sulfide concentration of the influent is changing slowly during the test period, the error attributed by the dwell time should not be pronounced enough to affect the material balance calculations.

The influent analysis remained constant in composition with regard to pH, Settleable Solids, and Total Solids. During the test period, the alkalinity of the solution decreased and the sulfide in the influent increased. These changes were attributed to higher strength tanning wastes coming from the clarifier than was present during the early stages of the test. The feed rate of the sulfuric acid was constant during the test run. As the alkalinity of the influent decreased, the pH of the effluent also decreased and a greater removal of sulfide was achieved.

The data on the suspended solids in the effluent is inconsistent with that observed in other runs. A possible explanation of this could be in the amount of lime carried with the influent. Particulate lime upon reaction with the sulfuric acid would become solubilized resulting in a net decrease in suspended solids. Table No. 19 shows data for the degasifier influent relating to suspended solids, settleable solids, total solids, and sulfide content as measured every 30 minutes during the material balance run. Table No. 20 shows data for the same parameters relating to the degasifier effluent and taken at the same time intervals.

The degasifier influent and effluent sulfide rates/minutes were calculated for each 30 minute interval. Table No. 21 lists the sulfide rates of the influent, the effluent, and for the sulfide enroute to the absorber by difference.

Samples from the caustic soda solution in the recirculation tank and at the absorber flue were taken at the same time intervals as from the degasifier influent and effluent. Analyses were made for specific gravity, temperature, pH, percent sodium hydroxide, and percent sulfide. The analytical results are in Table No. 22. From this data, the pounds of sodium hydroxide used and the pounds of sulfide absorbed were determined.

At the start of the test run, there was some sulfide present in the caustic soda solution. This is due to the mechanical configuration of the tanks. Some caustic soda-sodium sulfide solution remains in the tanks after emptying and is present for the next run. Density, temperature and volume measurements can be used in calculating the pounds of caustic soda and sulfide in the system. The data on the sulfide

TABLE NO. 23

MATERIAL BALANCE RUN - ABSORBER EXHAUST FLUE DATA

Sample Identity	1	2	3	4	5	6	7	8	9
Time	12:00	12:30	13:00	13:30	14:00	14:30	15:00	15:30	16:00
Temp. ^oF	82	96	100	106	108	108	110	110	112
Flow, cfm	490	450	360	330	320	320	390	380	430
Sulfide, as H_2S/cu Meter by Zinc Acetate Method	150*	150*	197	186*	268	276*	400	400	1306
By Instrumentation	-	-	248	-	337	-	450	450	-
Sulfide, lbs Discharged	0.13	0.14	0.18	0.21	0.23	0.27	0.35	0.70	

* Data by extrapolation

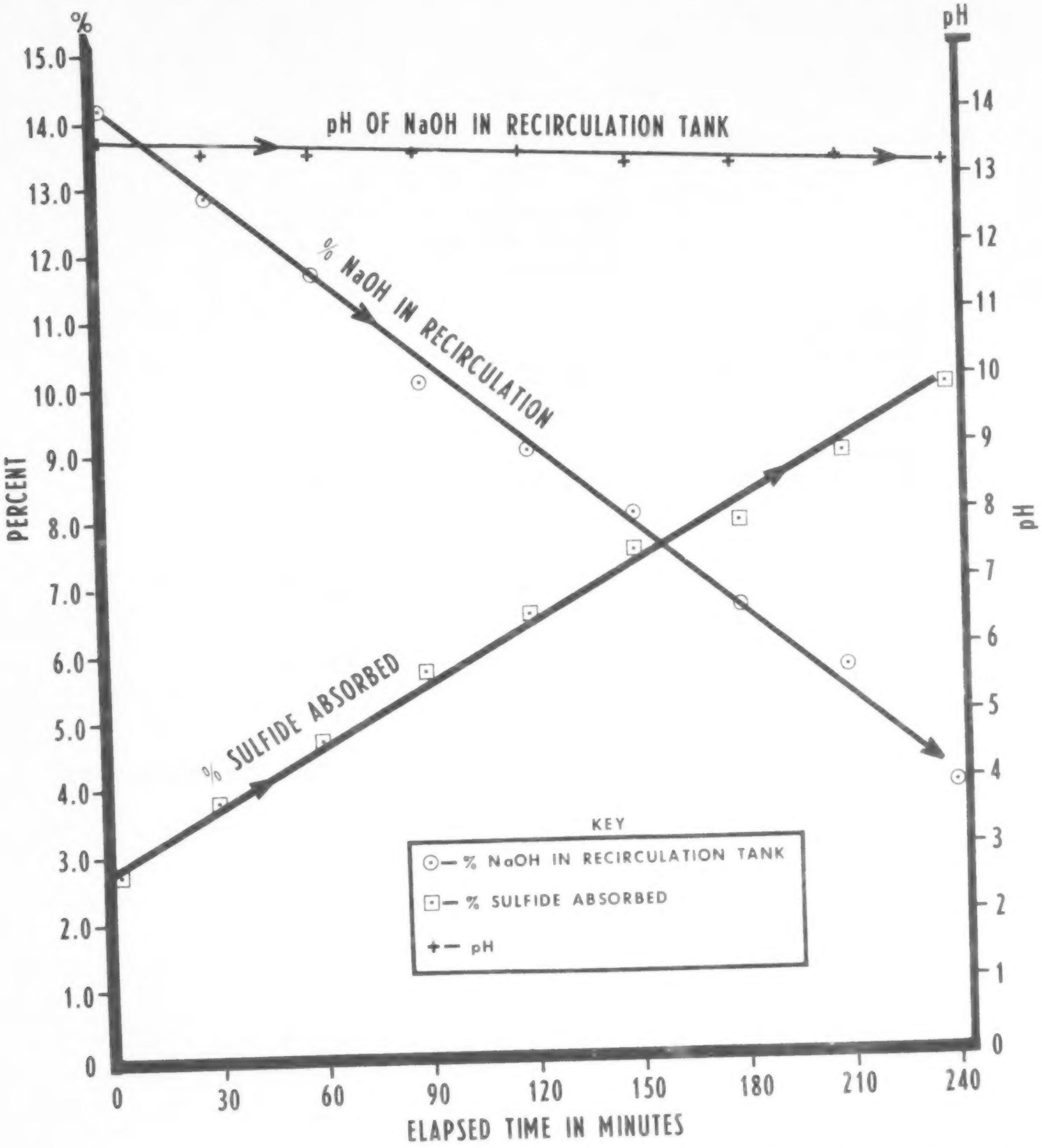


Figure 15. Absorber analysis: caustic soda consumed, sulfide absorbed, pH of circulation caustic tank vs. elapsed time.

TABLE NO. 24

MATERIAL BALANCE OF THE SULFIDE RECLAMATION SYSTEM

	Calculated Using Average Sulfide	Calculated From Data Tables
Sulfide in Degasifier Influent, lbs	548.77	538.0
Sulfide in Degasifier Effluent, lbs	14.23	14.7
Sulfide to Absorber by Difference, lbs	534.54	523.3
Sulfide Absorbed by Analysis, lbs	526.4	526.4
Sulfide Flue Emission, lbs	8.14 (by difference)	2.2 (by analyses)
Sulfide Recovered by Absorption, %	95.9	97.8
Sulfide in Flue Emission, %	1.48	0.4
Sulfide in Degasifier Effluent, %	2.59	2.7
Total % =	99.97	100.9

take-up and the decrease in the caustic soda conforms to a near stochiometric ratio.

The air discharge from the absorber was sampled and analyzed using the same time schedule. Air flow and temperature readings were also made. The analysis for sulfide in the air discharge was obtained at several but not all data points. The missing data points were estimated and shown along with other data in Table No. 23. At the end of the four hour test the concentration of the caustic soda is decreased to the extent that the amount of hydrogen sulfide being discharged with the air analyzes to be in excess of 1,000 mg/l.

Data on the hydrogen sulfide in the exhaust air was measured by chemical analysis using the Zinc Acetate Absorption Method and also using the Research Appliance Sulfide Analyzer. The chemical data was consistently lower and was considered to be more accurate. The Research Appliance apparatus is satisfactory for operational control.

Figure No. 15 illustrates the decrease in sodium hydroxide, the increase in sulfide absorbed, and the decrease in the pH of the recirculation caustic soda used during the material balance run.

The material balance data summarized in Table No. 24, shows that the sulfide can be removed from the degasifier influent when acidified to a 5.0 - 5.5 pH. Approximately 98% of the sulfide in the tannery wastewater is recoverable for reuse in the unhairing process. The small amount of effluent reflected in the data is due to improper pH levels of 6.3 to 7.3 at the beginning of the run. Sulfates in the effluent show an increase due to the addition of sulfuric acid for pH adjustment. The loss of sulfide to the atmosphere and the effectiveness of the caustic soda absorption could be improved by the use of a larger absorption column, a larger caustic soda recirculation tank, higher caustic concentration, or by use of two absorption columns in series.

SECTION 10

PROTEIN COAGULATION AND SEDIMENTATION: EFFECT ON POLLUTION LOADING

Acidification of the degasifier influent to a 5.0 - 5.5 pH which is necessary for sulfide reclamation causes coagulation of solubilized proteins. During the evaluations of the sulfide system, comparative analyses were made of the pollution loading benefits of removing the coagulated proteins by sedimentation of the degasifier effluent. The initial design for the wastewater treatment plant at Blueside Company had scheduled secondary sedimentation; however, it was not incorporated into the plant as constructed.

Table No. 25 shows the reductions to be achieved over the time periods involved as related to the tannery's weekly production of hides. The 1976 data shows a 25% BOD_5 reduction by sulfide removal. Further protein removal effects a total 60% BOD_5 reduction in pollution loading. Composite samples of the degasifier influent and effluent were analyzed. The composite samples consisted of grab samples taken every thirty minutes during a four hour sulfide reclamation run. The degasifier effluent sample was split into two samples. One was used for analysis immediately, the second was allowed to settle for four hours. The supernatant liquid was drawn off for analysis. The residual protein solids were blotted with absorbent paper, air dried and then analyzed.

The reductions in pollution loading by the removal of coagulated proteins represents large savings to the company as an indirect discharger. Correspondingly, for a tannery with a similar sulfide system as a direct discharger, the decreases in the pollution parameters would greatly simplify a secondary treatment process.

The sale of the recovered protein may be doubtful, however, the sludge produced by sedimentation could have value as a fertilizer. As wastewater treatment system expands and chromium recycle is a reality, the protein would perhaps have an economic value. The protein sedimentation at the Blueside Company represents removal of coagulated proteins from the total tannery effluent.

TABLE NO. 25

PROTEIN COAGULATION AND SEDIMENTATION: EFFECT ON POLLUTION LOADING

Parameter, mg/l	1971 Operation				1975 Operation				1976 Operation			
	Influent	Effluent	Effluent without Proteins	% Removal Efficiency	Influent	Effluent	Effluent without Proteins	% Removal Efficiency	Influent	Effluent	Effluent without Proteins	% Removal Efficiency
pH*	9.5	5.3	5.3	--	8.7	5.3	5.3	--	8.2	5.5	5.5	--
Sulfide	126	3.5	0.0	100	1,395	44	21	98	1,107	13	10	99
Alkalinity to pH 5.5	--	--	--	--	--	--	--	--	3,834	0	0	100
Sulfates	--	--	--	--	4,802	9,156	8,950	(87)**	5,687	9,872	10,004	(76)**
Total Solids	21,740	24,100	21,260	2.2	30,590	34,560	22,560	26	35,820	37,960	22,100	38
Suspended Solids	2,210	2,240	0	100	4,820	5,520	315	94	6,520	6,560	1,420	78
Settleable Solids,	--	--	--	--	9	375	1	--	150	850	0	100
BOD_5	--	4,210	1,640	61	4,800	4,733	2,435	49	7,867	5,917	3,185	60
COD	--	7,340	3,440	53	3,160	11,738	4,155	68	15,625	12,660	3,260	79
Cr_2O_3	--	--	--	--	354	362	26	93	555	512	19	97
Oil and Grease	--	645	5	99	--	--	--	--	320	1,032	19	94

* Standard Units
** Increase due to $CaSO_4$ Formation

TABLE NO. 26

EFFECT OF pH ON PROTEIN SEDIMENTATION

AND

ANALYSIS OF PROTEIN SEDIMENT

Unit: mg/l unless otherwise stated

Effect of pH on Protein Sedimentation

Parameter	Control						
pH *	9.2	6.0	5.0	4.0	3.0	2.0	1.0
Total Settleable Solids	15	380	400	420	320	230	190
Supernatant Liquor							
Suspended Solids	2,950	200	300	300	300	300	300
Total Solids	22,400	27,000	29,200	17,400	30,100	33,100	70,300
pH *	9.3	6.3	5.2	4.3	3.3	2.4	1.8
Density, °Baume, 72°F	2.0	2.0	2.5	2.5	2.5	3.0	5.0
Cr_2O_3	520	32	38	82	51	44	25
Cr^{6+}	nil	nil	nil	nil	nil	nil	nil

* standard units

TABLE NO. 27

ANALYSIS OF PROTEIN SEDIMENT

Parameter	%
Moisture (air dry basis),	95.2
Total Solids,	4.8

Solids Composition (air dry basis)	%
Nitrogen Kjeldahl	3.38
Protein Equivalent	19.0
Oil & Grease	10.0
Sulfates	2.61
Chlorides	0.60
Calcium	1.64
Cr_2O_3	2.74
Cr^{+6}	Nil

Research conducted on protein recovery (19) showed that one pound of protein could be recovered from each 7 to 9 gallons of unhairing liquor sampled from a hide processor tannery process. Considering 1,200 gallons of unhairing liquor from each of 12 process batches per day at one pound of protein yield for each eight gallons of liquor, the amount of protein sediment attributable to the hairburn liquors would be 1,800 pounds per day.

Protein precipitation as reported began at 6.0 pH and continued precipitation down to about 3.8 pH. Most proteins precipitated between 4 and 5 pH. At pH 4.2, the protein solution appeared to act as a buffer. Further acid addition did not precipitate the proteins completely with small amounts remaining in the supernatant solution.

In order to determine the effect of pH on protein sedimentation, liter quantities of the clarifier effluent were acidified using sulfuric acid to varying degrees ranging from 6.0 to 1.0 pH and allowed to settle in an Imhoff cone. The settleable solids were recorded. The supernatant liquor was decanted and analyzed for total solids, suspended solids, and chrome content. The protein sediment from an acidification to 5.0 pH was blotted with absorbent paper and air dried. The protein sediment was analyzed for Kjeldahl nitrogen and factored to determine protein content. The air dried sediment was analyzed for oil and grease, sulfates, chlorides, and chromium.

Tables 26 and 27 show the results of pH variation on sedimentation and a protein sludge analyses, respectively. The data results from taking a five gallon sample of the clarifier effluent which was kept under agitation to allow representative liter samples to be taken for the experiment. Following acidification to the various pH levels, the samples were allowed to settle for four hours.

As the pH decreases, the settleable solids will increase until a 4.0 pH is achieved. Further acidification causes a decrease in settleable solids. This may be due to hydrolysis of the protein which occurs at 2.0 pH in the absence of sufficient salts to prevent acid swelling from occurring. The density of the supernatant liquor is 2° Baume and salinity concentrations of 6° Baume are required to prevent hydrolysis of proteins at 2.0 pH. The $^{\circ}$Baume of the clarified effluent increases from 2.0° at a 9.2 pH to 5.0 $^{\circ}$Baume at a 1.0 pH. The supernatant liquor becomes clearer up to a 4.0 pH and progressively milkier in appearance as 1.0 pH is approached. The total solids in the supernatant liquor will increase to 5.0 pH, decrease to a minimum at 4.0 pH, and increase to a maximum at 1.0 pH. This indicates that protein sedimentation would be optimum at 4.0 pH and that hydrolysis of the protein is occurring at 1.0 pH. The pH of the supernatant liquor was rechecked four hours after acidification and shows slight reductions in acidity. The suspended solids and the chrome content in the supernatant liquor are substantially reduced by acidification and settling.

The coagulated protein is amber in color at 6.0 pH and changes progressively to a whiter product as acidification to 1.0 pH proceeds. Analyses conducted on the protein sediment show 19% protein, 10.0% Oil and Grease, 2.61% Sulfate, 0.60% Chloride, 1.64% Calcium, and 2.74% Chromium, as Cr_2O_3.

Sedimentation of the protein would increase the sludge solids quantities for removal to landfill by approximately 2,150 pounds. Current daily sludge removal to landfill requires 43,000 pounds at 50% solids to be removed. The sludge is dewatered in filter presses. The sludge results from the processing of 200,000 pounds of hides/day. Protein sedimentation for removal would increase the sludge solids to 45,150 pounds. Since a dumpster of sludge for landfill contains 15,000 pounds, there should be no additional landfill costs.

Using the 1976 data from Table No. 25, the economies shown in Table No. 28 could be effected by protein removal. Credit is taken for sewer surcharges based on flow, BOD_5, and Suspended Solids.

TABLE NO. 28

ECONOMIC EVALUATION OF PROTEIN SEDIMENTATION ON MUNICIPAL SEWER SURCHARGE

Parameter	Surcharge without Sulfide Reclamation	Surcharge with Sulfide Reclamation And Protein Removal
Flow	$ 3,550	$ 3,550
BOD_5	2,358	910
Suspended Solids	7,190	1,306
Monthly Surcharge	$ 13,098	$ 5,766
ANNUAL SURCHARGE	$157,176	$69,192
NET SAVINGS:		$87,984

SECTION 11

ECONOMIC EVALUATION OF THE SULFIDE RECLAMATION SYSTEM AND WASTEWATER TREATMENT PROGRAM

The sulfide reclamation equipment cost estimated in 1968 is essentially accurate and listed in Table No. 29. Today's costs would be substantially higher based on the inflation trend of the last few years. Table No. 30 is a comparison of the 1970 economies of the sulfide system with the estimated economic evaluation for 1976.

The original labor cost estimates of 1970 were low. They indicated labor requirements of 300 man-days for a 250 day year operation with an annual cost estimate of $6,000 or 1.2 men per year.

Supervision and fringe benefits were not included in the overall labor cost estimates, nor was the expense of heating the system included. The estimated cost for electrical useage was also too low. Depreciation of equipment was estimated at $15,300 per year in the 1970 evaluation. The estimated chemical costs and useage requirements were low, and in addition, the expense for freight was not considered.

A net operating cost for the sulfide reclamation-reuse system in 1970 was set at $37,700 without consideration of freight costs. When recalculated with a 350 day year, the cost is equivalent to $25 per 1,000 hides processed.

The 1976 economic evaluation of the sulfide reclamation system shows higher labor costs resulting from six years of inflation and a change to an around-the-clock operation of the system over a 350 day year, requiring 2.4 man-years for its operation.

Costs for supervision, fringe benefits, more expensive replacement parts, maintenance, heating, and greater electrical requirements are included in the 1976 evaluation. An increase in depreciation expense is also indicated and based on the replacement of capital items during the past three years. The chemical quantities and cost are shown in the 1976 evaluation with and without freight expenses included.

TABLE NO. 30

ANNUAL ESTIMATED ECONOMIC EVALUATION OF SULFIDE RECLAMATION SYSTEM
ORIGINAL (1970) vs CURRENT (1976)

	ORIGINAL (1970)					CURRENT (1976)				
Item	Units	Annual Amount	Unit Cost	Sub Total	Annual Costs	Annual Amount	Unit Cost	Sub Total	Annual Costs w/o Frt.	Annual Costs w/Frt.
DIRECT COSTS										
Labor	man-days	300	$20	$6000		4 men @ 60% of their time, year round		$25208		
Supervision	-	-	-	-			Lump sum	2250		
Fringe	-	-	-	-				5492		
Maintenance	Lump Sum			2000				5349		
Gas	-	-	-	-				588		
Electricity	Kwh	2.5×10^5	0.015	3700		3.441×10^5	@$0.02543	8750		
Total Direct Costs					$11700				$47637	$47637
INDIRECT COSTS										
Depreciation of Equipment	20%			$15300				$21400		
Laboratory Supplies	-	-	-	-				250		
Total Indirect Costs					15300				21650	21650
CHEMICAL COSTS						Material:	Cost	w/Frt.		
Sulfuric Acid	tons	750	*40.	30000		2750	38.00	45.49	104500	125098
Sodium Hydroxide	tons	500	*80.	40000		740	140.00	150.00	103600	111000
Total Chemical Costs					70000					
TOTAL ANNUAL OPERATING COSTS					$97000				$277387	$305385
Income from Reclaimed Sulfide	tons	860	*69.		$59300	967	290.00	411.00	28430	397437
NET GAIN (OR LOSS)					($37700)				$3043	$92052

Original Basis: 6000 hides/day, 250 operating days/year

Basis: Average 21700 hides/week/350 days/year 18x8 hr. shifts/wk or 21700 ÷ 6 = 3617 hides/day

*Chemical Freight Costs not included

NOTE: Current Estimate has been calculated with and without Chemical Freight Costs to St. Joseph,MO

TABLE NO. 29

SULFIDE RECLAMATION SYSTEM EQUIPMENT COSTS

EQUIPMENT AND MATERIALS	AMOUNT
Feed pumps to degasifier (2)	$ 7,000
Acid feed pump	2,000
Recirculation pump	1,500
Caustic soda feed pump	1,500
Degasifier Tower	25,000
Absorber Tower	5,000
Automation Control System	7,000
Chemical Storage Tanks	10,000
Air Blowers (2)	10,000
Dahl tube and flow indicator	3,000
TOTAL COSTS	$72,000

An estimated net gain of $92,052 per year with the operation of the sulfide reclamation system is the result of savings in material costs, but primarily the result of a savings in freight costs. This equates to a net gain of $84.84 per 1,000 hides with uninterrupted operation of the system.

Table No. 31 cites the cost of the sanitary landfill operation for sludge removal.

A recapitulation of total wastewater treatment costs for the Blueside Company is shown in Table No. 32. Costs included are the sewer surcharge (for primary/secondary wastewater treatment) by the municipality and sanitary landfill charges for sludge disposal.

The estimated net gains expected from sulfide reclamation, chrome recovery reuse, and protein sedimentation removal (not yet operational) are considered in the 1976 economic evaluation. The net operating cost of the wastewater treatment systems at Blueside Company is stated as $120,272, which amounts to a net cost of $0.095 per hide processed.

The chemical treatment of sulfide by chlorination or hydrogen peroxide is expensive and prohibitive, except when its use is for the final removal of small quantities of sulfide. With proper operation of the sulfide reclamation system at a pH of 5.0 - 5.5, the use of chlorine or hydrogen peroxide to negate residual sulfide in the wastewater to a maximum of 10 ppm, as required by the municipal ordinance, would not be required.

TABLE NO. 31

SANITARY LANDFILL CHARGES AND QUANTITIES

Basis: Removal of 3 sludge dumpsters/day for six days/week for a 50 week year or a total of 900 x 15,000 pounds loads per year or 75 x 15,000 pounds loads per month.

MONTHLY CHARGE

Minimum Charge: 40 loads x $70 =	$2,800.00
+ Dumpster Maintenance =	200.00
Sub-total	3,000.00
+ 35 loads x $55 =	1,925.00
Total Monthly Total	$4,925.00
ANNUAL LANDFILL CHARGE	$59,100.00
ANNUAL LANDFILL QUANTITIES:	13,500,000 pounds @ 50% solids

The tannery operates 18 eight-hour shifts out of 21 potential shifts per week. The downtime for cleaning of the sulfide recovery system's degasifier is scheduled during the 21st and 1st shift periods at which time tannery wastewater flow of sulfide-bearing waste is zero. Flow into Blueside Company's wastewater treatment system and the municipal sewer is virtually stopped.

Table No. 33 shows the estimated cost of hydrogen peroxide to remove 40 ppm of residual sulfide and the average of 1,360 ppm sulfide present in the wastewater.

TABLE NO. 32

WASTEWATER TREATMENT COSTS

		Annual Amount	
Direct Costs			
Labor	6 men x 2080 x $ 5.56	$ 69,389	
Supervision		14,600	
Fringe		16,798	
Maintenance	Lump Sum	21,000	
Electricity	8.242 Kwh X10^{5}X0.02543	20,959	
	Total Direct Costs		$142,746
Indirect Costs			
Depreciation of Equipment		86,000	
Laboratory Services and Supplies		5,250	
	Total Indirect Costs		91,250
Waste Handling Costs			
Estimated sewer surcharge when municipal secondary treatment is on stream		157,176	
Sanitary Landfill charges for sludge removal		59,100	
	Total Waste Handling Costs		216,276
TOTAL ANNUAL OPERATING COSTS			450,272
Credit from Sulfide Reclamation System		92,000	
Credit from Chrome Recovery System		150,000	
Estimated credit from sewer surcharge economies when coagulated proteins are removed from degasified effluent		88,000	
	Total estimated income of pollution control projects		330,000
Net Cost of Wastewater Treatment at 21,700 hides/week for a 50 week year, the cost would be $0.095/hide			$120,272

TABLE NO. 33

HYDROGEN PEROXIDE COST ESTIMATE

Condition	Sulfide System Operational	Sulfide System Not Operational
Average Sulfide in Effluent, ppm	40	1360
Daily Effluent Volume, gallons	300,000	300,000
Sulfide needed to be oxidized, allowing 10 ppm to city sewer, lbs	75	3380
pH Range	5 - 7	8 - 9
Cost/pound 50% Hydrogen Peroxide	$0.2125	$0.2125
Stoichiometric Ratio of 50% Hydrogen Peroxide to Sulfide	2 : 1	8 : 1
Pounds of Hydrogen Peroxide (50%)	150	27,040
Cost Estimate per day	$42.50	$5,746.00
Cost per hide, 3617 hides per day	$0.0118	$1.59

*Proper operation of the sulfide reclamation system at 5.0 - 5.5 pH results in no sulfide in the wastewater flow to the municipal sewer. The choice of 40 ppm is for calculation comparisons of hydrogen peroxide to chlorine.

TABLE NO. 34

CHLORINE COST ESTIMATE

Condition	Sulfide System Operational	Sulfide Not Operational
Average Sulfide in Effluent, ppm	40	1,360
Daily Effluent Flow, in gallons	300,000	300,000
Sulfide needed to be oxidized, allowing only 10 ppm to city sewer, lbs	75	3,380
Cost/Pound Chlorine	$0.075	$0.075
Stoichiometric Ratio of Chlorine to Sulfide in effluent oxidation	10:1 minimum 15:1 maximum	10:1 minimum 15:1 maximum
Pounds of Chlorine Required	750 minimum 1,125 maximum	33,800 minimum 50,700 maximum
Cost Estimate per day	$56.25 to $84.38	$2,535 to $3,802.50
Cost per hide based on 3617 hides per day	$0.0156 to $0.0233	$0.70 to $1.05

*Proper operation of the sulfide reclamation system at 5.0 - 5.5 pH results in no sulfide in the wastewater flow to the municipal sewer. The choice of 40 ppm is for calculation comparisons of chlorine to hydrogen peroxide.

Table No. 34 shows the estimated cost of chlorine useage at the same two levels of sulfide content as used in the hydrogen peroxide cost estimate -- with and without the system operational.

Without the sulfide system operational, the cost of removing an average of 1,360 ppm to the 10 ppm required by ordinance would be $1.59 per hide for hydrogen peroxide useage and $1.05 per hide for chlorine useage. With the sulfide system operational and presuming an average of 40 ppm residual in the tannery wastewater, the cost comparison of removing the sulfide would be $0.0118 per hide for hydrogen peroxide useage and from $0.0156 to $0.0233 per hide for chlorine, dependent on the stichiometric ratio required.

The lower cost of hydrogen peroxide with the sulfide system operational is because the stoichiometric ratio requirement in wastewater at a pH range of 5 - 7 is 1:1. Proper operation of the sulfide reclamation system at a 5.0 - 5.5 pH, coupled with scheduling of downtime for the system's cleaning, will eliminate the need for expensive useage of chemical elimination of sulfides using either hydrogen peroxide or chlorine.

The chemistry of the hydrogen peroxide and chlorine reactions with sulfide is covered in the appendix, "Sulfide Chemistry".

SECTION 12

PROPOSED SYSTEM MODIFICATIONS

SULFIDE RECLAMATION SYSTEM

Two plans for reducing the downtime in cleaning the degasifier and overflow towers are under consideration and are outlined in the following proposals and schematics.

The first proposal, Figure No. 16, shows the installation of conical shaped trays installed in the existing degasifier. The liquid depth in the tower would remain the same, but at the apex of each conical tray a 6 inch diameter drain would be added with the necessary valving.

Air diffusers, parallel to the side walls of the degasifier, would still be used on each tray, but additional orifice openings and caps would be provided on diffusers to reduce clean-out frequency.

A full set of replacement check valve type air diffusers would be kept in stock for installation while the tower is open for cleaning. This would reduce the cleanout time, as the dirty diffusers would be cleaned during the interim period between tower clean-outs.

Additional spray heads, with piping capable of handling a higher water volume, would be installed in the top of each tray section to assist in clean-out.

In addition, a second absorber would be installed in series with the first one to eliminate H_2S flue emission.

A conical bottom and larger drain pipes at the base of the overflow tower will assist in the cleanout and are depcited in the schematic.

The second proposal, Figure No. 17, shows a degasifier with low liquid level trays. The low liquid level trays could be of the type designed by Koch Engineering Company. Flexitrays are valve-type trays consisting of perforated decks upon which round movable caps are mounted. The caps, which operate as check valves, are approximately 2 inches in diameter and have a limited lift capability accomplished by either a hold-down cage or by integral guide legs with lift stops.

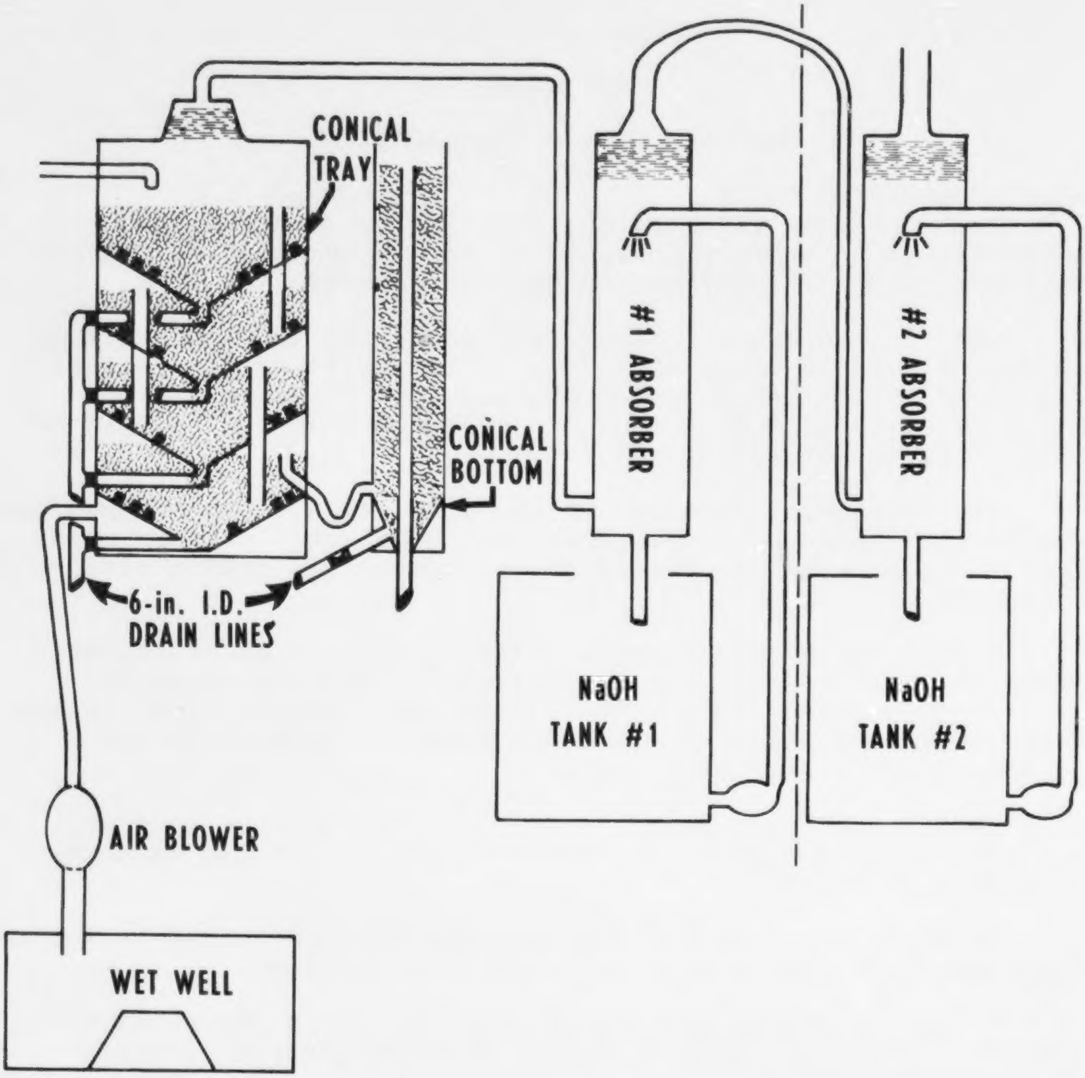

CONICAL TRAY
CONICAL BOTTOM
6-in. I.D. DRAIN LINES
#1 ABSORBER
#2 ABSORBER
NaOH TANK #1
NaOH TANK #2
AIR BLOWER
WET WELL

Figure 16. Proposed modification of sulfide reclamation system.

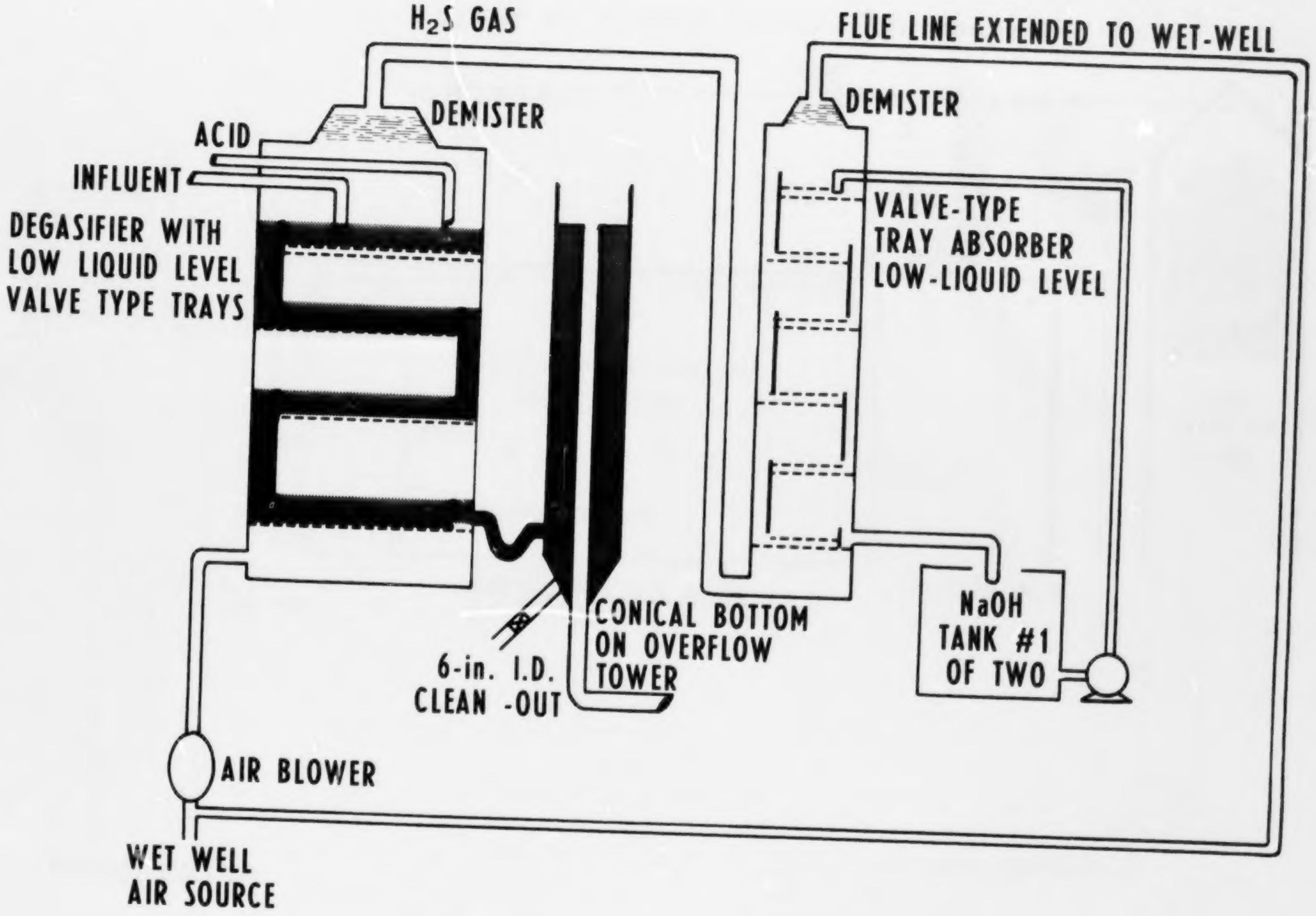

H_2S GAS
FLUE LINE EXTENDED TO WET-WELL
DEMISTER
DEMISTER
ACID
INFLUENT
DEGASIFIER WITH
LOW LIQUID LEVEL
VALVE TYPE TRAYS
VALVE-TYPE
TRAY ABSORBER
LOW-LIQUID LEVEL
NaOH
TANK #1
OF TWO
CONICAL BOTTOM
ON OVERFLOW
TOWER
6-in. I.D.
CLEAN -OUT
AIR BLOWER
WET WELL
AIR SOURCE

Figure 17. Alternate design of sulfide reclamation system.

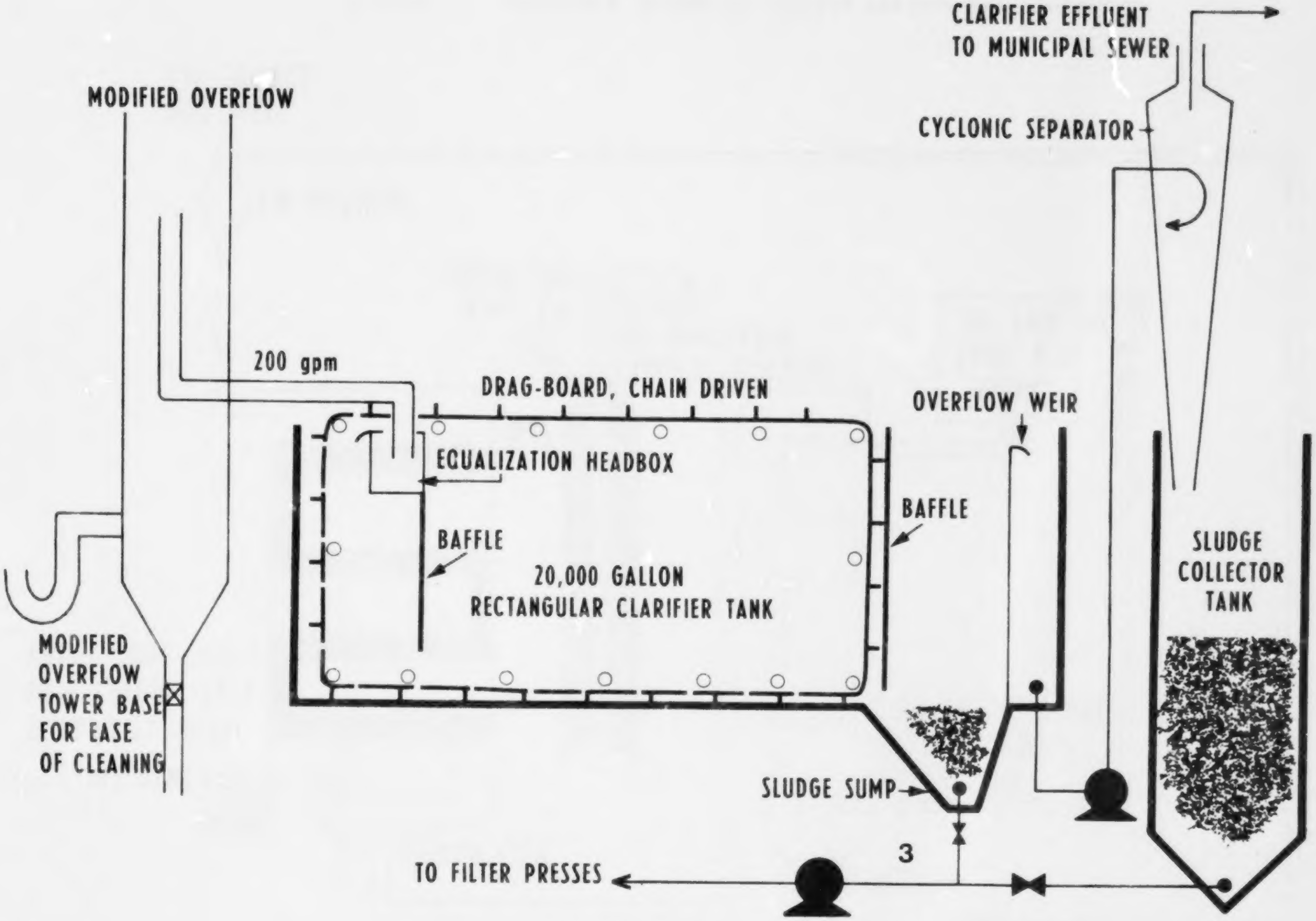

CLARIFIER EFFLUENT
TO MUNICIPAL SEWER
CYCLONIC SEPARATOR
MODIFIED OVERFLOW
200 gpm
DRAG-BOARD, CHAIN DRIVEN
OVERFLOW WEIR
EQUALIZATION HEADBOX
BAFFLE
BAFFLE
20,000 GALLON
RECTANGULAR CLARIFIER TANK
SLUDGE
COLLECTOR
TANK
MODIFIED
OVERFLOW
TOWER BASE
FOR EASE
OF CLEANING
SLUDGE SUMP
3
TO FILTER PRESSES

Figure 18. Schematic protein sludge removal.

The valves, made of different metal gauges, would be installed in alternating rows of light and heavy caps, parallel to the outlet weir, and would provide good vapor distribution over a wide range of air flow rates. At lower air flows, the lighter valves would lift to an open position. But as the air flow rate increased, the heavier weight valves would progressively open wider, eventually to their full open position. Even at the lowest air flow volume, air would flow upward through the crevices around the valves and would prevent leakage into the air blower.

Tray gasketing would not be necessary, not only because of the air flow upward through the crevices which would prevent leakage, but because of the lower liquid level's reduced downward force exerted on the valves. Tray gasketing, nevertheless, is available.

The number of trays required would be increased dependent upon the retention time necessary.

An additional low liquid level tower of proper dimension equipped with identical valve-type trays would be used as an absorber. Fresh caustic soda would flow into the top tray of this unit and flow countercurrent to the H_2S/air vapor.

The emergent solution at the bottom of this unit would move to tankage as sodium sulfhydrate or sodium sulfide solution in caustic soda, dependent upon the number of trays used. The flue from the absorber would be eliminated as all gas would return to the wet well and be recycled.

PROTEIN SEDIMENT REMOVAL PROPOSAL

Figure No. 18 is a schematic for the collection of degasifier effluent into a rectangular clarifier from a modified overflow pipe in the overflow tower. Modification of the overflow pipe would be required to have sufficient headroom to allow gravity flow of degasified effluent into the reservoir.

The effluent would be pumped from the clarifier into a separator (cyclonic or sludge blanket type) allowing further protein sludge to be removed. The clarified effluent would flow to the municipal sewer. The protein sludge would flow into a sludge receiving tank from which it would be pumped to a filter press for dewatering prior to disposal.

CHROME RECOVERY AND REUSE

Chrome recovery and reuse was not a part of this project. Its adoption will further reduce pollution loadings. The minimization of chrome in the tannery wastewater will lower the COD and produce a less bulking sludge for sanitary landfill. The elimiation of acidic components from the tannery effluent will result in a higher pH existing in the equalizing tanks prior to the hair screen and in the clarifier. This will decrease odor potential.

The chrome recovery and recycling at Blueside Company is based on reuse of exhaust liquor and excess amounts of liquor will accumulate which must be precipitated.

Indications are that a savings of $150,000 per year could be realized.

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APPENDIX A

SULFIDE CHEMISTRY

Hydrogen sulfide at normal temperature and atmospheric pressure is a colorless gas having the offensive odor of rotten eggs. It is a flammable gas and may explode on ignition at a temperature of 260°C (500°F) and a wide flammability range of 4.3% - 46% in air. The gas is highly toxic and at higher concentrations it paralizes the olfactory nerves preventing detection of the odor. It is a mild reducing agent and is oxidized under suitable conditions using chlorine, oxygen, sulfur dioxide, and sulfuric acid. It enters into reactions with many organic compounds. With solutions of heavy metals, (silver, lead, copper, manganese), hydrogen sulfide form metal sulfides.

Industrially, depending on the quantity and purity required, hydrogen sulfide is prepared by one of the following reactions:

Sulfur and hydrogen: $S + H_2 \rightarrow H_2S$

Sulfur and an alkali: $4\ S + 2\ NaOH + H_2O \rightarrow 2\ H_2S + Na_2S_2O_3$

Sulfide an an acid: $2\ NaHS + H_2SO_4 \rightarrow 2\ H_2S + Na_2SO_4$

Hydrogen sulfide may be supplied by on-site generators or in cylinder quantities in steel cylinders as a liquefied gas under its own vapor pressure of 252 psig at 70°F.

A number of producers of sodium sulfhydrate (NaHS) will purchase the hydrogen sulfide gas in large containers and allow the gas to escape from the cylinder under its own pressure into a packed column (or tray plate tower) where liquid caustic soda is caused to flow. The reactions that take place are as follows:

Reaction No. 1: $NaOH + H_2S \rightarrow NaSH + H_2O$

Reaction No. 2: $NaSH + NaOH \rightarrow Na_2S + H_2O$

In the presence of excess NaOH, reactions 1 and 2 take place simultaneous. As additional H_2S is fed into the Na_2S, the reaction goes to completion as follows:

TABLE NO. 35

PHYSICAL PROPERTIES OF HYDROGEN SULFIDE (Ref. 17)

Molecular Weight	34.08
Boiling Point, °C	-59.6
Melting Point, °C	-82.9
Tripple Point at 0.23 atm, °C	-85.5
Density	
Gas at 21.1 °C, g/l	1.43
Liquid at boiling point, g/ml	0.993
Specific Gravity	
Gas at 15°C (air = 1)	1.1895
Liquid, d^{60}_{4}	0.96
Critical Temperature, °C	100.4
Critical Pressure, atm	88.9
Critical Density, G/cm^3	0.349
Expansion Ratio, liquid at Boiling Point to Gas at 21.1°C	1:674
Solubility in Water of Gas at 26.7°C wt. %	0.32
Specific Heat of Gas at Constant Pressure at 21.1°C, cal/g mole (°C	8.2
Heat of Vaporization, cal/g mole	44.63
Heat of Fusion, cal/g mole	568
Viscosity of Gas at 0°C, cp	0.01166
Autoignition Temperature, °C	260
Flamable Limits in Air, volume %	4.3 - 46.0

Reaction No. 3: $Na_2S + H_2S \rightarrow 2\ NaHS$

The end product of the commercially absorbed H_2S is NaHS, or sodium sulfhydrate. Since the hydrogen sulfide is fed into the absorber from a cylinder under its own pressure of 252 psig, the system is airless.

The sulfide reclamation system at Blueside Company makes use of a controlled air flow to carry the liberated hydrogen sulfide from the degasifier to the absorber. The air flow volume is controlled as related to the hydrogen sulfide liberated from the degasifier influent to ensure that the H_2S concentration in air is below the 4% lower explosion limit. The properties of hydrogen sulfide are listed in Table No. 35.

At Blueside Company, hydrogen sulfide is formed in the degasifier by acidification of the sulfide bearing wastewater influent to a 5.5 - 5.0 pH using sulfuric acid. The reaction is as follows:

$$\text{Effluent sulfides} + H_2SO_4 \rightarrow \text{Effluent sulfates} + H_2S$$

The conversion of the hydrogen sulfide to sodium sulfide is limited to reactions 1 and 2 above.

The removal of sulfides from product flows by selective solvent absorption in packed towers or plate towers is common place in the chemical and petro-chemical industries. It is a safe operation as is the sulfide reclamation system at the Blueside Company.

The solubility of hydrogen sulfide in water at any given temperature is based on two phenomena; Henry's Law and the ionization of hydrogen sulfide as a weak acid. Henry's Law, simply stated, defines the distribution of a gas between a liquid solvent and a gas phase as a constant proportion at a given temperature. Henry's Law may be written as $pa=H\ Xa$ where pa is the mole fraction of the component in the gas above the liquid, and Xa is the mole fraction of the component in the liquid. A simplified approximate ratio may be stated $H = pa/Xa$ where pa = ppm H_2S in the air and Xa = ppm in the liquid.

The hydrogen sulfide in the water in the relationship is only the sulfide as hydrogen sulfide present. Since hydrogen sulfide is a weak dibasic acid, the degree of disassociation is dependent on pH. At a low pH 5.0, the ionization of the hydrogen sulfide is repressed and approximately 99% of hydrogen sulfide is not in the ionized state. In Section 7 it was stated that one theoretical tray was required to liberate the hydrogen sulfide from the liquid. Henry's Law resulted in 0.00672 pounds of sulfide remaining in the liquid as opposed to 0.02 pounds as reflected by the data. The hydrogen sulfide in the vapor phase above the liquid based on the data was 2.21 pounds - 0.02 pounds = 2.19 pounds. Based on Henry's Law, the amount above the liquid would be 2.21 - 0.00672 pounds = 2.2033 pounds, or 99.7% of the hydrogen sulfide liberated from the liquid.

The ionization of hydrogen sulfide in water proceeds in two steps in accord with the following equations:

$$H_2S \leftrightarrows SH^- + H^+$$

The ionization constant of this reaction is:

$$10^{-7} = \frac{(SH^-)\ (H^+)}{H_2S}$$

The second ionization step is:

$$SH^- \leftrightarrows S^= + H^+$$

The ionization constant of this reaction is:

$$10^{-15} = \frac{(S^=)\ (H^+)}{SH^-}$$

At any pH, the state of ionization of the sulfide can be determined. In the influent to the sulfide reclamation plant at pH 9.0, the calculations are as follows:

$$10^{-7} = \frac{(SH^-)\ 10^{-9}}{H_2S}$$

$$\frac{SH^-}{H_2S} = \frac{10^{-7}}{10^{-9}} = 10^2$$

The ratio of sulfhydrate to hydrogen sulfide is 100:1

$$10^{-15} = \frac{(S^=)\ 10^{-9}}{(SH^-)}$$

$$\frac{S^=}{SH^-} = \frac{10^{-15}}{10^{-9}} = 10^{-6}$$

The ratio of sulfide to sulfhydrate is therefore 1: 1000000

From these equations, the ionization of the sulfide at the significant pH's for the sulfide reclamation can be calculated. Table No. 36 lists the concentration of ions in the solution at various pH levels.

TABLE NO. 36

IONIZATION OF HYDROGEN SULFIDE

Source	pH	H_2S	SH^-	$S^=$
Influent	9.0	10^{-2}	1	10^{-6}
Acidified Influent	5.0	10^{2}	1	10^{-10}
Acidified Influent	6.0	10	1	10^{-9}
Absorber	12.0	10^{-5}	1	10^{-3}
End point of NaOH Analysis	8.2	$10^{-1.2}$	1	$10^{-6.8}$

For the degasifier influent at pH 9.0, the sulfide is present primarily as the sulfhydrate ion. Very little sulfide is present. Approximately 1% is present as hydrogen sulfide. Acidification to pH 5.0 results indicate that hydrogen sulfide is not ionized and is the dominant sulfide present, sulfhydrate is present at approximately 1% level, and the sulfide $S^=$ concentration is less than 1 ppm. At pH 12 in the absorber, the sulfide is present predominantly as the sulfhydrate ion. Hydrogen sulfide is present in the range under 10 ppm and about 0.1% of the sulfide is present as sulfide ion $S^=$. At pH 8.2, the sulfide is present primarily as the sulfhydrate ion. Approximately 5% of the sulfide is present as hydrogen sulfide and the amount of the sulfide $S^=$ ion is less than 1 ppm.

If commercially available sodium sulfide (Na_2S) were placed in solution at a concentration of 10% in water, the ionic concentration of SH^-, $S^=$ and OH^- would be as follows:

For hydrolysis of $S^=$

$$\text{I} \quad S^= + H_2O \leftrightarrows HS^- + OH^- \qquad Kh = \frac{10^{-14}}{10^{-15}} = 10$$

$$HS^- \leftrightarrows H^+ \quad S^= \qquad K_2 = 1 \times 10^{-15}$$

$$H_2O \rightleftarrows H^+ \quad OH^- \qquad Kw = 10^{-14}$$

$$\text{II} \quad H^+ + S^= + H_2O - HS^- + H^+ + OH^-$$

$$Kn = \frac{(HS^-)(H^+)(OH^=)}{(H^+)\ (S^=)}$$

$$Kw = (H^+)\ (OH^-)$$

$$K_2 = \frac{(H^+)\ (S^=)}{(SH^-)}$$

$$Kh = \frac{Kw}{K_2}$$

Equations I and II are the same equation.

Since Na_2S and NaSH total to be 1.28 molar concentration, let $SH^- = X$

Therefore $(S^=) = 1.28 - X$ and $(HS^-) = (OH^-)$ from equation I

$$Kn = \frac{(HS^-)\ (OH^-)}{(S^=)} \quad \text{or } Kn = \frac{X^2}{1.28 - X}$$

$$10 = \frac{X^2}{1.28 - X}$$

$$12.8 - 10X - X^2 = 0$$

Using the quadratic equation: $X = 10 - \frac{(100 + 4 \times 12.8)^{\frac{1}{2}}}{-2}$

$$X = 1.148 \text{ Molar}$$

$$SH^- = 1.148 \text{ Molar}$$

$$S^= = 1.28 - 1.148 = 0.1318 \text{ Molar}$$

Therefore, a 10% sodium sulfide solution has the sulfhydrate ion present in a 1.148 molar concentration and sulfide $S^=$ ion present in a 0.1318 molar concentration, or a sulfhydrate to sulfide ratio of 8.7 to 1.

Using Henry's Law, it is possible to determine what pH level is necessary in the caustic soda recirculation tank to the absorber to maintain the H_2S escaping into the atmosphere below 100 ppm from a 10% sodium sulfide solution. Henry's Law constant for H_2S at 90°F is calculated to be 12.14 atmosphere molar $^{-1}$. If the limit of H_2S into the atmosphere is to be 100 ppm, then the partial pressure will be:

$$\frac{100}{1,000,000} = 10^{-14} \text{ atmospheres}$$

Therefore, the solution concentration must be:

$$Km = P_{H_2S}$$

where "m" is the molality, "K" is Henry's Law constant, and "P" is the partial pressure of H_2S. Calculating for m:

$$m = P_{H_2S} / K$$

$$m = \frac{10^{-4} \text{ atmosphere}}{12.14 \text{ atmosphere molar}^{-1}}$$

$$m = 8.234 \times 10^{-6} \text{ molar}$$

If H_2S is passed through the packing tower containing caustic soda solution to produce Na_2S and NaSH, the pH calculations require determining the hydrolysis steps for preparation of two equations which will then be solved using the quadratic equation.

Hydrolysis steps

$$S^{=} + H_2O \rightleftarrows HS + OH \qquad K_{h2} = \frac{Kw}{K_2}$$

$$K_{h2} = \frac{10^{-14}}{10^{-15}} = 10$$

$$HS^{-} + H_2O \rightleftarrows H_2S + OH^{-} \qquad K_{h1} = 10^{-14}$$

Assuming a concentration of 10% Na_2S, the molarity will be 1.28 molar.

For hydrolysis, Let $X = (HS^{-})$ and $Y = (OH^{-})$

Then: $1.28 - x = (S^{=})$

For hydrolysis of $S^{=}$

$$K_{h2} = \frac{(HS^{-})\ (OH^{-})}{S^{=}} = \frac{XY}{1.28-X}$$

For hydrolysis of HS^{-}

$$K_{h1} = \frac{(H_2S)\ (OH^{-})}{HS^{-}} = \frac{8.234 \times 10^{-6} Y}{X}$$

Therefore, the two equations for solving are as follows:

Equation I $10 = \frac{XY}{1.28 - X}$

Equation II $1.11 \times 10^{-7} = \frac{8.234 \times 10^{-6}Y}{X}$

To find the OH^- concentration needed or Y, rearrange the equations:

Equation II $X = \frac{8.234 \times 10^{-6}Y}{1.11 \times 10^{-7}} = 74.1Y$

Substituting Equation I $10 = \frac{74.1\ Y.Y}{1.28 - 74.1Y}$ or $12.8 - 74.1Y - 74.1Y^2=0$

Using the quadratic equation:

$$Y = + 741 - \frac{(741^2 + 4 \times 74.1)^{\frac{1}{2}}}{-2 \times 74.1}$$

$$Y = 0.0172\ M \quad \text{or} \quad (OH^-) = 0.0172M$$

$$pOH = - \log 0.0172M$$

$$pOH = 1.76$$

$$pH = 14.0 - 1.76$$

$$pH = 12.24$$

A pH of 12.24 for a 10% solution of sodium sulfide will assure no more than 100 ppm of H_2S into the atmosphere.

Oxidation of Sulfides

Manganous Sulfate has been used as the catalyst in aeration systems to convert sulfides to elemental sulfur and/or sulfates. The reactions proceed as follows:

$$2\ HS^- + O_2 + H^+ \xrightarrow{Mn^{++}} 2\ H_2O + 2\ S$$

or to sulfates

$$HS^- + 2\ O_2 \xrightarrow{Mn^{++}} SO_4^= + H^+$$

Hydrogen peroxide may be used as a method of controlling the sulfide content in an effluent. The hydrogen peroxide reacts on a stoichrometric basis at a range of 6 - 7 pH.

$$H_2S + H_2O_2 \xrightarrow[pH\ 6\ -\ 7]{Neutral} S^= + 2\ H_2O$$

Under strongly alkaline conditions, the chemistry shifts and four times as much hydrogen peroxide is needed:

$$S^{=} + 4\ H_2O_2 \xrightarrow[\text{pH 9.0}]{\text{Alkaline}} SO^{=} + 4\ H_2O$$

Therefore, the most economical utilization of hydrogen peroxide requires that the pH of the effluent be maintained between 6 - 7. With the degasifier down, the acidulation of the effluent would not be possible and the pH of the effluent would be in the range of 8.5 - 9.0 requring the 4:1 peroxide to sulfide ratio.

Chlorine is used to oxidize the sulfide, the reaction requires 8.87 parts of chlorine to 1 part of sulfide. The chlorine, however, reacts with other organic matter present in the effluent, so that 10 to 15 parts of chlorine may be consumed before the sulfur is completely converted to sulfate.

$$HS^{-} + 4\ Cl_2 + 4\ H_2O \longrightarrow SO_4^{=} + 9\ H^{+} + 8\ Cl^{-}$$

The addition of chlorine to an effluent depresses biological activity, virtually stopping the consumption of oxygen, until the chlorine residual has disappeared. During this period of suppressed biological activity, the stream acquires an oxygen reserve that will delay the reappearance of sulfide downstream. (14)

On pure sulfide solutions, chlorine converts the sulfide to sulfur requiring 2.2 parts chlorine to 1 part sulfide:

$$HS^{-} + Cl_2 \longrightarrow S + H^{+} + 2\ Cl^{-}$$

The elimination of sulfides in an effluent reduces the oxygen demand in the treatment plant and reduces the BOD_5 pollution loading of the wastewater resulting in a lower municipal sewer surcharge. Oxygenation of the sulfides in the treatment plant would produce thio-compounds through to sulfates:

$$S^{=} + O_2 \longrightarrow SO_2,\ SO_3,\ SO_4$$

Toxicology of hydrogen sulfide gas dictates care in personal safety and constant training for awareness of dangers. Blueside Company has signs dictating the potential presence of H_2S in all areas where the possibility exists. Respirators, gas masks, sensing devices, personal belt alarm units make for a safe-guard approach in tannery areas where sulfides are used. High ventilation rates of outside air through the potential areas has ensured an H_2S free plant.

The principal manifestation of H_2S poisoning is irritation.

a. Acute Poisoning

Hydrogen sulfide is detectable by odor at 0.5 ppm, and 10 ppm causes irritation and sensory loss. Concentrations above 50 ppm cause the following symptoms: painful conjunctivitis, appearance of a halo around lights, headache, anosmia, nausea, rawness in the throat, cough, dizziness, drowsiness, and pulmonary edema. Concentrations above 500 ppm cause immediate loss of consciousness, depressed respiration, and death in 30 to 60 minutes.

The threshold limit of exposure has been set at 10 ppm for an 8 hour day.

b. Chronic Poisoning

Prolonged exposure causes persistent low blood pressure, nausea, loss of appetite, weight loss, impaired gait and balance, conjunctivities, and chronic cough.

c. Prognosis

In hydrogen sulfide poisoning, if the patient survives for the first four hours, recovery is assured. (18)

APPENDIX B

ORIGINAL SPECIFICATIONS

1 SULFIDE STRIPPING SYSTEM

General

Furnish, install controls, instruments, and accessory equipment necessary for the operation of a sulfide stripping system, as specified herein.

The sulfide stripping system is to convert gaseous hydrogen sulfide mixed with air to sodium sulfide for process use. This is accomplished by blowing the hydrogen sulfide gas from the degasifying tower through an absorption tower, in which sodium hydroxide is being circulated. A chemical reaction will occur and the sodium hydroxide will be converted to sodium sulfide.

A hydrogen sulfide monitor will take samples from the exhaust air stream of the absorption tower and will indicate when the sodium hydroxide is converted to sodium sulfide. At that time, a new batch of sodium hydroxide will begin circulating. The sodium sulfide will be transferred to storage, and a new batch of sodium hydroxide will be made up in the empty tank.

The system will operate for eight hours per day initially, and later will operate 24 hours per day, except for infrequent shutdowns.

Data to be Furnished

Submit for approval six complete sets of shop drawings, showing details of construction and erection, and four complete sets of operating and maintenance instructions, including wiring diagrams.

Design

Scope

One supplier shall assume the responsibility for the sequence of operation of the sodium sulfide stripping system. This shall be a complete and operating system, including at least the following:

(a) Control cabinet and necessary relays
(b) Hydrogen Sulfide detector
(c) Timers for control system
(d) Horn and lights
(e) Level sensors with relays for batch tanks
(f) Solenoid operated valves

Process piping shall be installed by others. Solenoid and motor operated valves supplies under this section shall be installed by others as a portion of the process pipework. However, all responsibility for operation of these valves shall remain under this section.

Operation

The sequence of operation of the sulfide stripping system shall be as follows:

1. The system will be initiated by the "Start" push button, on the control cabinet, for continuous operation of the system until the "stop" push button is activated or by interrupting power to the cabinet.

2. The caustic feed pump and valve to fill batch Tank No. 1 shall be energized. Tank will fill to approximately 52.5 gallons with 25 percent caustic. Level will be fixed by a level probe called the intermediate level.

3. The intermediate level probe shall shut off the valve to batch Tank No. 1 and stop the caustic feed pump. The water valve to batch Tank No. 1 shall open to complete the makeup of 10 percent caustic. An upper level probe shall be fixed and close the water valve to Tank No. 1.

4. Upper level probe shall energize a relay to start the circulation pump. The circulation pump shall be locked in until the system "Stop" push button is activated or by interruption of power.

5. The upper level probe in batch Tank No. 1 shall open the circulation valves to and from batch Tank No. 1.

6. A caustic solution shall be made up in batch Tank No. 2 through a similar sequence and shall be held ready until called upon.

7. A hydrogen sulfide detector will monitor the exhaust gas from the absorption tower and alarm when the hydrogen sulfide content exceeds a preset limit. The

The alarm shall indicate that the sodium hydroxide has been converted to sodium sulfide.

8. An adjustable recycle timer shall be in the circuit parallel to the hydrogen sulfide detector and will start its cycle with each batch tank circulation system. This is provided to replace the hydrogen sulfide detector and will start its cycle with each batch tank circulation system. This is provided to replace the hydrogen sulfide detector alarm in case of failure of the detector. The timer shall also be able to be taken out of the circuit.

9. Upon indication of an alarm, a time delay relay shall be activated to confirm that the preset excess of hydrogen sulfide is escaping by taking another sample. A relay will then be energized by either the alarm or timer to close the circulation valve from batch Tank No. 1. Another time delay relay shall be actuated to drain the absorption tower before the circulation valve to batch Tank No. 1 shall be closed (the tower does not have to be completely drained). Immediately thereafter the circulation valves with batch Tank No. 2 shall open, transferring circulation from batch Tank No. 1 to No. 2.

10. If the transfer is not completed within an adjustable time limit and an excess hydrogen sulfide is detected, an audible and visual alarm shall go off. This will notify the operator of trouble in the sequence of operation.

11. The sodium sulfide drain valve from batch Tank No. 1 shall open and the sodium sulfide transfer pump shall start. When batch Tank No. 1 is empty, as determined by a low level probe, the sodium sulfide transfer pump shall stop and the sodium sulfide drain valve from batch Tank No. 1 shall close.

12. Batch Tank No. 1 shall then be refilled as in Steps 2 and 3 with fresh caustic solution and be held ready until called upon.

13. When the sodium hydroxide solution in batch Tank No. 2 has been converted to sodium sulfide as indicated by either alarm or time, the circulation shall be transferred to batch Tank No. 1 as outlined in Step 9, only switching from batch Tank No. 2 to No. 1. The cycle will repeat as in Steps 10, 11, and 12 only with batch Tank No. 2.

14. The system shall be continuous in operation, alternating between the batch tanks unless the sequence is stopped manually or by power interruption. In that case, the system shall be restarted manually, and through the relays will resume operation where it was stopped.

Control Cabinet

An electrical control cabinet shall be provided to house the sequencing control for the hydrogen sulfide stripping system. Cabinet shall conform to Joint Industry Standard with hinged door and latch and be for wall mounting. The door shall be gasketed to keep out dust and fumes. Cabinet exterior and interior shall be cleaned, primed, and finished in an enamel selected by the owner. Nameplates shall be black lamicoid with white filled lettering 0.25 inch in height.

The relays, except for level sensing specified elsewhere, shall be industrial duty equal to General Electric CR2790E or CR120J with 120-volt coils for continuous duty. Push button stations and selector switches shall be oiltight, heavy duty construction equal to General Electric 2940 for flush panel door mounting. An industrial type horn shall be provided. All control wiring shall be of industrial duty equal to 600 volts, Flaminol, installed in a workmanlike manner, with terminal strips, as necessary, cabled where necessary, and securely fastened to the cabinet interior by approved methods. All wiring shall be coded for ease of identification in trouble shooting.

An external fused disconnect shall be provided and mounted adjacent to the cabinet.

Hydrogen Sulfide Sampler Detector

The sampler detector for hydrogen sulfide concentration shall be an integral unit, complete with sampling pump, monitor, timer, and alarm control circuitry. The monitor shall be adjustable over the limits of 0.0025 to 25 ppm of hydrogen sulfide. Unit shall have automatically adjusted transmission through clean paper with built-in voltage regulator. Vacuum air pump shall have a capacity of 0 to 30 SCFH free flow continuous duty. A prefilter shall be provided for trapping particular matter. Alarm contracts shall be rated at 120 volts, 5 amperes, noninductive load. Sensitive/tape shall only advance when hydrogen sulfide exceeds a preset limit. This shall be part of a tape-saving feature which includes a sampling frequency adjustable from 1 to 60 minutes in intervals of one minute. The tape shall advance automatically after an alarm condition through an adjustable built-in timer. Analyzer shall be provided with 30 rolls of 60 foot punched tape, sensitized for hydrogen sulfide. A humidity jar shall be attached to the air inlet and the exhaust gases shall be passed through a soda and lime tube to scrub out any hydrogen sulfide that may have passed through the tape. The detector cabinet shall be for wall mounting, next to the control cabinet.

The hydrogen sulfide detector shall be Research Appliance Company, Allison Park, Pennsylvania, Catalog No. 2307-B, Model F-2-A AISI, or approved equal.

Level Sensors

The level sensors shall be of the probe type. Each shall consist of a probe holder with four No. 316 stainless steel probes and differential relays having built-in transformers for power supply isolation.

One probe on each holder shall be bare and extend to within 0.50 inch of tank bottom to serve as a "ground" electrode. A second probe shall extend to within one inch of tank bottom and be the low level probe. A third probe shall terminate at one-third tank capacity (about 50 gallons) and be the intermediate level. High level will be the fourth probe and extend within six inches of the top (150 gallons). The level probes shall be PVC coated to within one inch of the tip, for service in a 25 percent caustic solution.

The probe holder shall be supplied with a three inch pipe threaded connection to fit on the batch makeup tank.

Probe relays shall be mounted in the control cabinet. The relay types and contact arrangement shall be such that they will operate in accordance with the automatic sulfide stripping system.

The level sensing system shall be as manufactured by B/W Controls, Birmingham, Michigan, or approved equal.

Timers

The timers shall be of the adjustable time delay type. The time shall be adjustable from a knob on the front and the timers shall be flush panel mounted on the control cabinet.

Timers shall be Bliss Eagle Signal Company, Davenport, Iowa, Cycl-Flex, HP5 Series, or approved equal.

Solenoid Operated Valves

All process valves under the one inch pipe size shall be two-way type solenoid valves selected for the specific service. Valves handling caustic and alkaline sodium sulfide solutions shall have all-iron or stainless bodies with Teflon seats. Diaphragm, when used, shall be resistant to twenty-five percent caustic solution. Valves for cold water service shall have bronze bodies with stainless steel trim.

Valves shall be equal to Automatic Switch Company, Florham Park, New Jersey, ASCO, or approved equal.

Motor Operated Valves

Process valves one inch and over shall be ball valves with reversing electric motor operators. Valves shall be constructed of PVC, carbon steel or ductile iron, suitable for the service intended. Valve seals shall be molded Teflon or of other composition suitable for intermittent service. Motor operators shall be supplied in weatherproof housings and for operation on 120-volt, 60-cycle power. Valves shall be supplied with 150 pound ASA flanges.

Valves shall be equal to Worcester Valve Company, Worcester, Massachusetts, Econ-O-Miser with a Flow Mate operator, Hills-McCanna Company, Carpentersville, Illinois, McCannaseal with a Ramcon operator, or approved equal.

2 DEGASIFYING AND OVERFLOW TOWERS

General Requirements

Furnish all materials and equipment required for installation and satisfactory operation of the degasifying tower and overflow tower.

Data to be Furnished

The selected manufacturer shall submit structural calculations for the tower to the Engineer for approval. All calculations shall be stamped by a Registered Professional Engineer.

The tower shown on the drawings is illustrative and indicates only the design features to be incorporated. Special reinforcement, etc., is not shown. Piping orientation shall be as indicated on the drawings.

Submit for approval six sets of complete shop drawings showing details of construction and errection, and four complete sets of operating and maintenance manuals.

Design

The degasifying tower shall be provided for the removal of sulfides from the settled plant effluent. The effluent will be mixed with sulfuric acid and discharged into the top of the tower. Air will be introduced into the bottom of the tower and will flow upward through the tower thus removing the entrained hydrogen sulfide gas. The gas will be discharged out the top of the tower to the adsorbtion tower. The treated effluent will flow into an overflow tower where chlorination will be provided. The effluent will flow from this tower to the city sewer.

The four-stage degasifying tower shall be provided as indicated on the drawings. The settled effluent will be pumped at a rate of approximately 220 gpm to the top stage of the tower, at which point it will be mixed with concentrated sulfuric acid. Air will be provided by a positive displacement blower at a rate of 700 cfm at a maximum of 10 psig into a plenum at the base of the tower. The air will pass upward throughout the tower and pass out through a discharge line in the top of the tower. The tower shall be airtight.

Each stage will be provided with check valve type air diffusers. Each level will maintain a 3 foot 3 inch depth of liquid. Downward flow shall be allowed only through the downcomers. The waste will leave the tower through a 12 inch effluent in the bottom stage.

The degasifying tower shall be constructed of polyester resin and fiber glass or other suitable corrosion-resistant materials approved by the Engineer. The tank shall be structurally designed to withstand all possible load conditions including wind loads.

Minimum standards for towers made by hand lay-up shall be in compliance with Product Standard PS-122-C for Custom Contact-Moulded Reinforced Polyester Chemical Resistant Process Equipment issued by the U. S. Department of Commerce; and for towers fabricated by filament winding, shall be in compliance with the Proposed Product Standard for Filament Wound Reinforced Polyester Tanks being developed by the Society of the Plastics Industry.

The tower shall be provided with a six inch flanged inlet in the top stage along with a one inch connection for concentrated sulfuric acid. The effluent connection shall be 12 inches in the bottom stage. All interior piping shall be fiber glass or PVC. The air will enter through an eight inch connection in the base section. A 12 inch air outlet connection shall be provided in the top section. Each stage shall be provided with a six inch viewing port with a window, a 24 inch access manhole with a blank cover and a two inch connection to a drain. All flanges shall be standard ANSI Class 150 pound rated. All openings shall be reinforced for strength.

Each chamber shall be connected to the next one with a 12 inch diameter downcomer with a 24 inch funnel top section. They shall be deep enough in the solution so air will not escape upward through them. There shall be 80 air diffusers per chamber with a ball check valve built-in. They shall be made of a plastic that will not corrode and have an orifice adjustment so the head loss and air flow may be adjusted. The diffusers shall be Link-belt Adjust-air diffusers or approved equal.

A spray system shall be provided in each chamber to prevent possible foaming. The nozzles shall be of Everdur or approved equal as manufactured by Schutte and Loerting. It shall be possible to start and stop the system with an external valve. All piping shall be internal and made of fiber glass, PVC or other approved material that will resist corrosion. A minimum of four (4) nozzles shall be provided in each chamber. The piping shall be supported internally. The spray system shall not use more than 60 gpm. A strainer shall be used upstream to prevent clogging.

The waste shall leave the degasifying tower and go to an adjustable overflow tower. The overflow weir shall be adjustable over a range of 48 inches. This adjustment is required so that the waste will flow out but gases will not escape. The weir shall be a telescoping valve as manufactured by Rex Chainbelt, Milwaukee, Wisconsin and made of stainless steel parts within the tower. An electric motor operator shall be furnished with a weatherproof push button station at the base of the tower. The valve shall have a neoprene seal to prevent leakage of gas or effluent between the body and telescoping sections of the valve. After overflowing over the weir there shall be provided a chlorine contact chamber in the base as detailed on the drawings before going to the sewer. This adjustable weir tower shall be airtight and be provided with at least two six inch viewing ports near the surface. A steel ladder shall be attached to this so the viewing ports may be utilized.

Warranty

The degasifying and overflow towers shall be warranted to be of good quality and constructed with the best commercial practice. The towers shall be air tight to prevent the escape of hydrogen sulfide gas. Any material or workmanship that, within two years after delivery to the job site, is found to have been defective, shall be repaired or replaced by the manufacturer.

Alternate

The manufacturer shall submit an alternate price for providing tank insulation. It is anticipated that the wastewater will enter the tower at approximately 50°F and could be held in the tower a maximum of 64 hours with no inflow. Outside temperature can be expected to drop to -10°F. Insulation material should be sufficient to prevent freezing. Design calculations and samples of the insulation shall be submitted to the Engineer.

3 ABSORPTION TOWER

General Requirements

Furnish all materials and equipment required for installation and satisfactory operation of the absorption tower.

Data to be Furnished

If the selected manufacturer proposes to furnish specially fabricated equipment, the Engineer shall require submittal of structural calculations for the tower for approval. All calculations shall be stamped by a Registered Professional Engineer. If a standard tower is offered, calculations will not be required.

Submit for approval six sets of complete shop drawings, showing details of construction and erection, and four complete sets of operating and maintenance instruction.

Design

An absorption tower shall be provided to convert hydrogen sulfide gas from the degasifier to liquid sodium sulfide. A solution of sodium hydroxide will be cycled through the tower to convert the gas to sodium sulfide.

The absorption tower indicated on the drawings is strictly diagrammatical and is intended only to indicate the required design features. Standard manufacturers' absorption towers, if they meet the requirements of this specification, will be acceptable.

The tower shall be suitable for handling hydrogen sulfide gas and 10 percent liquid sodium hydroxide solution. The tower design shall incorporate but not be limited to the following features:

1. Inlet - outlet connections
2. Positive seal on tank overflow
3. Sodium hydroxide spray system
4. Packing material
5. Tower drain
6. Diffuser plate

It is the intent of these specifications that the equipment operate as described herein.

The gas shall enter the side near the base of the tower. The gas will pass through at a rate of approximately 700 cfm at 3.5 psig minimum to 5.5 psig maximum. (This is the rate of discharge of the positive displacement blower connected to the degasifying tower.) The gas will pass through a contact bed counter to the flow of sodium hydroxide. The contact bed shall force intimate mixing between the gas and liquid. The sodium hydroxide shall be uniformly distributed over the packing through non-clogging spray nozzles. The nozzles shall be designed so the entire system can handle 20 gpm flow at 20 psig. The nozzles shall be stainless steel. An adequate number of nozzles shall be provided so that the entire surface area is in contact with the spray within a vertical distance of two feet below the bottom of the nozzles. The nozzles shall be easily removed for inspection and cleaning. An adjustable air seal shall be provided in the base so all gases must pass through the packing and not be short circuited to the batch tanks located below.

The absorbtion tower shall be constructed of molded reinforced polyester or other suitable materials that will resist corrosion and physically able to withstand the process involved. Materials shall be subject to approval of the Engineer. The tower shall be air tight.

Minimum standards for towers made by hand lay-up shall be in compliance with Product Standard PS-122-C for Custom Contract-Molded Reinforced Polyester Chemical Resistant Process Equipment issued by the U. S. Department of Commerce; and for towers fabricated by filament winding shall be in compliance with the Proposed Product Standard for Filament Wound Reinforced Polyester Tanks being developed by the Society of the Plastics Industry.

The tower shall be provided with 12 inch inlet and exhaust connection flanges. There shall also be provided a 1¼ inch flange for the sodium hydroxide inlet, a four inch flanged connection for the drain to the batch tanks and a two inch connection with a valve for draining the tower. An additional 18 inch flange shall be provided with a blank flange for access. All openings shall be reinforced for strength and all flanges shall be standard ANSI Class 150 pound rated. The tower shall be approximately four foot in diameter and 10 foot high and shall be designed to operate when filled with sodium hydroxide.

The packing material shall be Koch Flex rings or approved equal. This packing shall be supported on a diffuser plate which will distribute the gas up through the packing and allow the caustic solution to pass down through the batch tank for recycling. The diffuser plate shall be constructed of a material that will withstand the process. The caustic solution specified in another section will be fed to the tower at the rate of 20 gpm.

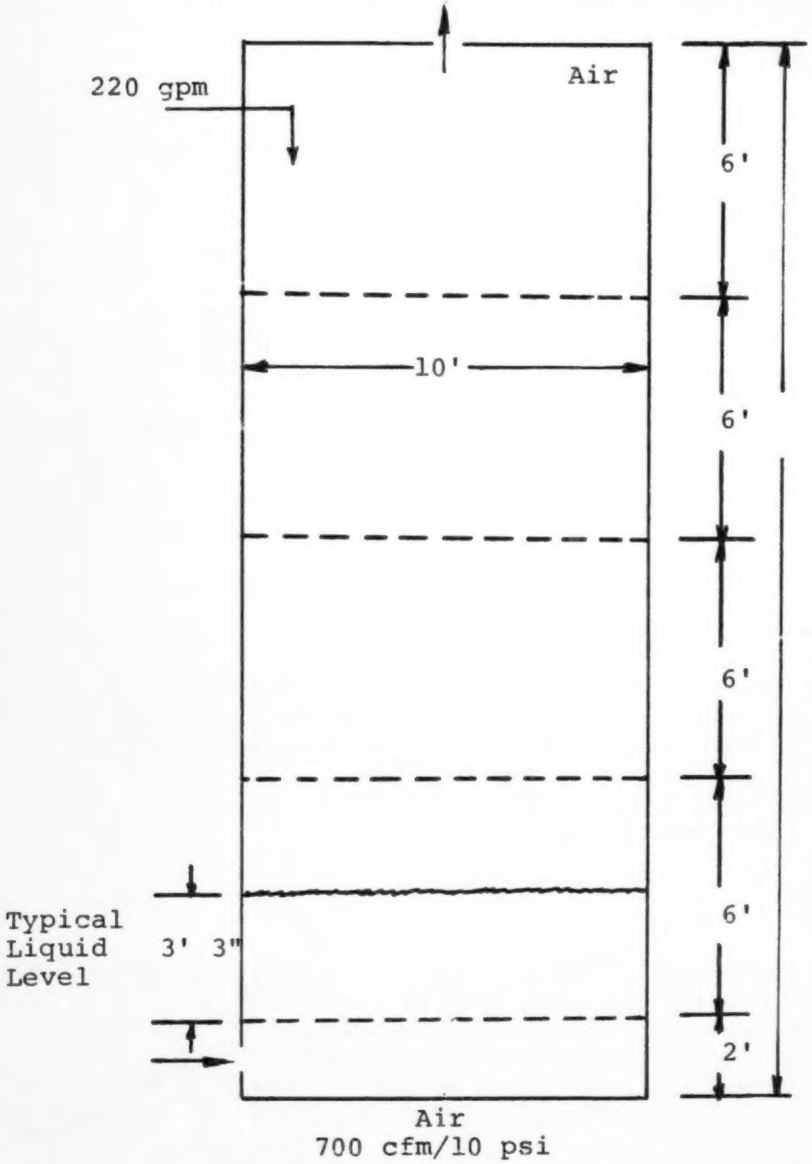
The manufacturer shall supply the 12 inch exhaust pipe with a tap for 0.25 inch sample line to the hydrogen sulfide detector. Pipe shall be PVC.

Warranty

The absorption tower shall be warranted to be of good quality and constructed in conformance with the best commercial practice. Any material or workmanship that within two years after delivery to the job site, is found to have been defective, shall be repaired or replaced by the manufacturer.

APPENDIX C

DEGASIFIER DESIGN CALCULATIONS


220 gpm
Air
6'
10'
6'
6'
6'
Typical
Liquid
Level
3' 3"
2'
Air
700 cfm/10 psi

Where P = Press (psi)
R = Radius (inches)
and t = Thickness (inches)

TOWER DESIGN

Girth Stress: $S_G = \frac{PR}{t}$

Design S_G = 200 psi (Max.)
Wall thickness $t = \frac{13.5}{2000} (60) = 0.405"$

OR

½" Nominal for maximum condition of flood

Axiel Stress
From Blower w/full tower
$\Sigma \uparrow$ 8 psi x 11,310 (in.)^2 = 90,500#
$\Sigma \downarrow$ Vessel Dead Weight = 6,000#
Fluid - 7400 (8.33) 1.2 = 74,000#
= 80,000#
Net Axiel - 90,500 - 80,000 = 10,500#
or 0.93 psi on Bottom Tray
Therefore: Vessel should have 8 tie down lugs for 1315# ↑ each.

VESSEL

Size: 10' 0" I.D. x 26' 0" High
Wall: Circumference 31.4'
Bottom: Area 78.54 ft.^{2}
Weight: @ ½" nominal wall @ 4.45#/ft.^{2}
Wall = 26 x 31.4 x 4.45 = 3,640#
Bottom & Trays 78.5 x 5 x 4.45 = 1,750#
Tor 78.5 x 1.1 x 3.5 = 300#
Fittings & Inner Piping = 200#
Net vessel weight 5,890#

FLUID

Volume (585 gals./ft) @ 3 ft, 3 in. = 1,900 gal./tray
4 trays - 7,400 gallons normal operation
Total Tower - 585 x 26 - 15,200 gal.
Specific Gravity: Assume not to exceed 1.2
Static Pressure: Per tray = 1.2 x .434 x 3.25 = 1.69 psig
: Flood Condition 1.2 x .434 x 26 = 13.5 psig

AIR SIDE

To supply given 700 cfm and 10 psig of air, Ref: Link belt 644 x 15 adjust air loss and flow data.

a

a. At 80 diffusers/tray:

$$\frac{700\ \text{cfm}}{80\ \text{Diffusers}} = 8.75\ \frac{\text{cfm}}{\text{Diffuser}} \quad \text{At Design}$$

8.75 = 0.1 psi Drop @ 12 orifices open/diffuser
= 0.15 psi Drop @ 8 orifices open/diffuser
= 0.30 psi Drop @ 4 orifices open/diffuser

b. Pressure drop/tray
1.8 psi @ 12 Orifices/diffuser
1.9 psi @ 8 Orifices/diffuser
2.0 psi @ 4 Orifices/diffuser

c. Four tray pressure drop
12 orifices/diffuser = 7.2 psi
8 orifices/diffuser = 7.6 psi
4 orifices/diffuser = 8.0 psi

APPENDIX D

SULFIDE RECOVERY SYSTEM OPERATION

A. System Operating Procedure

1. Ensure the wastewater level in the sedimentation-equalization basin is at about 12 inches above the outlet orifice in the clarifier rim weir.

2. Be sure all drain valves are closed on degasifying tower and in the overflow tower.

3. In the overflow tower set the adjustable overflow outlet pipe at 16 feet - 4 inches above the lowest tray's diffuser deck.

4. Start the wastewater pump and adjust the flow to about 190 gpm. Fill the degasifying tower and the overflow tower until the liquid level in the lowest tray of the degasifying tower is at 46 inches. This should require about 33 minutes. Observe the liquid level in the sight glass. When the proper liquid level has been reached, start the air compressor.

5. While waiting for the degasifying tower to fill, turn on the spray water in the scrubber on top of the degasifying tower. Adjust the flow to about 5 gpm. Start the gas absorption tower. Check the recirculating flow of NaOH. This should be between approximately 15 - 18 gallons per minute.

6. After starting the air compressor, start the acid feeding system. Do not operate the acid feed system when the air compressor is off because inadequate mixing may take place with the result that strong acid may damage the degasifying tower.

7. After starting the air compressor, observe the liquid level in the degasifying tower sight glass. The liquid level should drop to about the level of downcomer. Allow about 10 minutes for the conditions to stabilize. Adjust the height of the adjustable overflow outlet until the liquid in the sight glass is about 4 inches above the level of the downcomer.

8. After the degasifying tower has been in operation for about 10 minutes, a sample of wastewater should be taken from the upper tray and checked for pH value. If necessary, adjust the acid feed rate to obtain a pH between 5.0 and 5.5 in the upper tray.

   The pH should then be checked from time to time and the acid feed rate adjusted as necessary. If the wastewater pump rate is changed, the acid feed rate will also have to be changed. Therefore, changes in the wastewater pumping rate should be kept to a minimum.

9. To shut down the system:

   (a) Turn off the acid pump.
   (b) Shut off the main pumps.
   (c) Shut off the air compressor.
   (d) Open the degasifying tower drains.
   (e) Open the overflow tower bypass.
   (f) Shut off the scrubber spray system.
   (g) Shut off the H_2S absorption system.
   (h) After the degasifying tower is drained, flush it out using the water spray system within each level.